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INTERNATIONAL CHEMICAL SERIES

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TECHNICAL GAS AND FUEL ANALYSIS

McGraw-Hill Book Company

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TECHNICAL GAS AND FUEL ANALYSIS

BY

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McGRAW-HILL BOOK COMPANY, Inc.

239 WEST 39TH STREET, NEW YORK

6 BOUVERIE STREET, LONDON, E. C.

1913

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THE·MAPLE·PRESS·YORK·PA

PREFACE

With the increased demand for the economic utilization of fuels has come an increased necessity for accuracy in testing both the raw fuel and the manner of its utilization. Our knowledge has recently been greatly extended by the investigations conducted by the Committee on Calorimetry of the American Gas Institute, the International Photometric Commission, the Joint Committee on Coal Analysis of the American Chemical Society and the Society for Testing Materials, the Bureau of Mines and the Bureau of Standards.

The author has aimed to present the conclusions of these committees and also to indicate where there has been marked dissent from them. He desires to express his especial appreciation to Professor O. L. Kowalke of the University of Wisconsin for his courtesy in revising the chapter on Determination of Heating Value of Gas; to Professor S. W. Parr of the University of Illinois for suggestions on Calorimetry and Chemical Analysis of Coal; and to Dr. H. C. Dickinson of the Bureau of Standards for his suggestions on Calorimetry.

Ann Arbor, Michigan,
August, 1913.

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TECHNICAL GAS AND FUEL ANALYSIS

CHAPTER I

SAMPLING AND STORAGE OF GASES

1. Difficulties Involved.—The problem of obtaining a representative sample of a gas for analysis presents in many cases more difficulties than the analysis itself. If the gas flowing through a main were of perfectly uniform composition throughout its cross-section and also throughout its length the problem would simplify itself to the introduction of a tube through which a portion of gas might be removed for analysis. The proposition becomes at once more complicated when it is necessary to sample gases which have not passed through any adequate mixing chamber and which usually travel through the main or flue in pulsations of widely varying composition. Ocular evidence of this condition is afforded by a glance at the average smoke stack with its pulsing billows of smoke. If it is desired to determine not only the composition of the fixed gases but also the amounts of suspended solids, tar particles, water globules, etc., the problem becomes one of great complexity, capable frequently of only partial solution. This question is discussed separately in Chapter IX.

2. The Problem of a Fair Sample.—Gases should be sampled as close as possible to the point of the reactions which are to be studied, thus minimizing errors due to leakage of air or gas, deposition of solids or secondary reactions. Gases travel through straight pipes in an irregular succession of waves of rather a spiral form, the velocity being greatest at the center of the pipe and least next to the walls. The shape of the wave is altered by every bend, branch or other change in the pipe and the point of maximum velocity is also shifted. The temperature of gases from hot furnaces also varies throughout the cross-section of the

conducting pipe, being usually hottest where the velocity is greatest and coldest next to the walls and in dead bends.

It is in general advisable to sample from a point of approximately average velocity and temperature, but it is not possible to find a single point from which a truly representative instantaneous sample can be drawn. It is necessary to extend the sampling period over a time which will on the theory of probabilities allow so great a series of gas waves to pass the sampling tube that the resulting sample will be truly representative. A small volume of gas can therefore only be considered a representative sample when it has been drawn from a practically homogeneous mass of gas—a condition which is rather closely fulfilled in illuminating gas which has been purified and further made uniform through mixing and diffusion in a large gas holder. The condition is not fulfilled in producer or chimney gases.

No fixed time can be set as the most desirable for a single gas sample. If the sample is being taken from chimney gases which are supposed to be the same from one hour to another, the sampling process may very well extend over one hour or six hours. The longer the period the more nearly will the sample be an average one. The same thing holds true for illuminating gas coming from a holder, but it would not hold true for producer gas from a single producer nor for illuminating gas from a single retort, for these gases vary continuously in composition, each fresh charge of coal commencing a new cycle. When dealing with gases of this sort it is necessary to start and stop the sampling with reference to some definite point in the cycle. A truly proportional sample of a constantly varying gas cannot be obtained without rather elaborate precautions.

3. Materials for Sampling Tubes.—Sampling tubes must be of a material which will not react with the gases and change their chemical composition. Iron, and in general metals, cannot be used at high temperatures. Iron reacts with carbon dioxide quite rapidly at 400° F., producing carbon monoxide and oxide of iron. It also reacts readily with oxygen. An oxidized pipe will react with hydrogen causing that gas to disappear as water at equally low temperatures. Pipes with rough surface will induce a rapid catalytic decomposition of such gases as ammonia and some of the less stable hydrocarbons at a rather low red heat.

The best materials for sampling tubes are glass, quartz or porcelain. These tubes should be protected by a wrapping of asbestos in the form of paper or twine and should be slipped into an iron jacket which takes the strain off the tube and prevents sudden temperature changes. Glass begins to soften about 600° C. or 1100° F. and on long exposure to a red heat devitrifies and ultimately cracks spontaneously on cooling. Porcelain will stand about 1000° C. or a little over 1800° F., but at higher temperatures the glaze commences to soften. Unglazed porcelain will stand a higher temperature and special refractory mixtures may be obtained which will not soften at 1700° C. or 3000° F., but such tubes are apt to be porous and should only be used if proved to be free from leaks. Fused quartz is in some respects admirable as a material for sampling tubes, since its coefficient of expansion is so small that it never cracks because of temperature changes. It will stand 1100° C. or about 2000° F. without softening but on long heating tends to become crystalline and brittle. The ordinary electroquartz tubes are often porous and should be carefully tested.

4. Types of Sampling Tubes and Their Use.—The simplest form of sampling apparatus consists of a single tube through whose open end the gases are aspirated. When sampling from a large flue the sampling tube is sometimes closed at the end and perforated at various points along its length with the expectation that gas will be drawn uniformly through the holes at intervals across the flue. A device of this sort usually fails of its purpose and is often less efficient than a single tube. If the perforations are all of the same diameter they will allow the same amount of gas to pass through only in case the suction is the same on each. This condition can be attained in practice only by making the perforations small and the suction high so that it will be practically as great at the far as at the near end of the sampling tube. But such small holes stop quickly with dust and are not practicable.

A better device to secure a more uniform sample from the gases of a flue is shown in Fig. 1. It consists of a bundle of glass tubes of the same diameter but of varying lengths which are wired together and slipped into an iron pipe not quite so long as the shortest glass tube. The glass tubes are cemented into this with neat

Portland cement in such a manner that their ends next the threaded joint are all even and about 2 in. from the end of the iron tube. This may readily be accomplished in the following manner. Plug the threaded end of the iron pipe with a cork and stand it vertically on the corked end. Plug one end of each of the glass tubes with putty and stand them in the iron tube with their lower ends resting on the cork. Fill the iron tube for 3 in. with a paste of Portland cement and water and allow to stand for twelve hours to harden. The sampler is finished after removing the cork and putty by screwing onto the iron pipe a cap which is provided with a 1/4-in. nipple to which convenient connection may be made. The suction required to draw a slow stream of gas through a smooth tube 2 ft. long is only slightly more than that required for a 1-ft. tube. The empty space at the end of the pipe acts as a mixing chamber and allows a fairly satisfactory sample to be drawn through the nipple.

The sampling tube is to be inserted in the flue in such a way

FIG. 1.—Multiple gas sampling tube.

that there will be no leakage around it. An iron gas main may be drilled and tapped to receive a threaded nipple into which the sampling tube is luted when in use and which is closed by a cap when not in use. When a hole must be cut through a brick wall a threaded nipple may be cemented permanently into the wall and closed, when not in use, with a cap. If only a single sampling tube is used it should be inserted to about the point of mean velocity of the gases, a subject which is discussed in Chapter IX. Where a multiple sampling tube of the above type is used it should be inserted so that the longest tube reaches at least to the center of the flue.

It is frequent but bad practice to connect the sampling tube and the aspirator by a rubber tube. Rubber is softened and burned by hot gases and yields gaseous products which contaminate the sample. It also dissolves tar and hydrocarbon vapors and even permanent gases like ethylene in sufficient amount to materially change the character of the gas. Furthermore, even

the best rubber is never gas tight but always allows some leakage. It is usually necessary to use a small amount of rubber tubing in making connections, but its use should be restricted to lengths of only an inch or two where it serves as a connector between glass tubes. When thus used a copper wire should be twisted tightly around the rubber where it slips over the glass tube to ensure a tight joint.

5. Aspirators.—The commonest form of aspirator consists of a bottle or tank initially filled with water which flows slowly out and is replaced by the gas. With this form of aspirator the suction constantly decreases as the head of water drops and therefore the flow of gas slackens, which is a disadvantage. This may be overcome by making the gas as it enters pass down through a central tube and then bubble up through the water on the principle of the Marriotte bottle, but unless the water of the aspirator has been previously thoroughly saturated with the gas this process is certain to change the composition of the gas very materially. The extent of the error introduced by failure to observe this precaution is discussed later. A film of heavy paraffine oil is sometimes poured on the water of the aspirator bottle to prevent interaction between the water and the gas. Such an oil-film does not, however, prevent the interaction and does not even make it much slower. If oil is used it should be at least as heavy as a lubricating oil so that it will not give off any appreciable volume of vapors which even in small amount will cause difficulty in the estimation of oxygen by phosphorus. Oil should not be used when the gases sampled contain hydrocarbons, since these are quite soluble in heavy mineral oils.

Where frequent samples are to be drawn a pair of aspirator tanks as shown in Fig. 2 are to be recommended. Tanks to hold approximately a cubic foot should have the cylindrical portion 12 in. in diameter and 12 in. high with the cones each 6 in. high. They may be made of galvanized iron and will be strong enough with merely soldered seams if they are not knocked about too much. The ends of the cones terminate in short 1/2-in. nipples soldered in. The lower end of the tank carries screwed to this nipple a 1/2-in. cock F, and beyond this another 1/2-in. nipple with a hose union. The upper nipple carries a 1/2-in. tee on whose side-arm is an ordinary 1/4-in. gas cock E, and on whose

upper end is a cap tapped for a 1/4-in. pipe. This pipe, cut the length of the tank, is threaded into the cap from the inside before the latter is in place so that when screwed together the 1/4-in. pipe runs the whole length of the tank and projects through the cap enough to receive the gas cock D. With a pair of bottles of this sort the water flows from one to the other and is not exposed to the air so that it remains saturated with the gas.

If a water or steam line is at hand an injector may be employed as an aspirator. It is desirable in most cases to have the suction a slight and steady one, a condition not readily attained with injectors running only to a small per cent. of their capacity. It is well to have the injector open more widely than is necessary to furnish the suction required and to have on the line an automatic water seal relief valve as indicated at E in Fig. 3 which will suck in air at the inlet of the aspirator if the suction rises too high.

6. Solubility of Gases in Water.—The solubility of gases in water varies with the temperature and the pressure. For our treatment it will be sufficient to assume that the gas is always under atmospheric pressure and at ordinary room temperatures. Under these circumstances the solubility of the common gases is as follows:

SOLUBILITY OF GASES IN WATER

Expressed as the volume gas dissolved by unit volume water at the temperature of the experiment when in contact with the pure gas at atmospheric pressure.

	59° F.	77° F.
Carbon dioxide	1.070	0.826
Oxygen	0.036	0.031
Nitrogen	0.019	0.016
Carbon monoxide	0.027	0.023
Methane	0.039	0.033
Ethylene	0.147	0.119

When mixed gases are in contact with water the amount of each gas dissolved will be in direct proportion to its volume and its solubility. Thus the composition of pure water saturated with air at 59° F. would be

Composition of air, per cent.	Volumes of gases in 100 vols. water	Percentage composition of gas dissolved by water
CO_2..... 0.04	0.04×1.07 =0.043 vols. CO_2	1.9
O_2.....21.0	21.0 ×0.036=0.756 vols. O_2	32.9
N_2.....79.0	79.0 ×0.019=1.500 vols. N_2	65.2
	Total dissolved gas =2.299 vols.	100.0

The composition of the gases in water saturated with chimney gases may be calculated in the same manner.

Composition of gas, per cent.	Volumes of gases in 100 vols. water	Percentage composition of gas dissolved by water
CO_2.....10	10×1.07 =10.70	85.0
O_2.....10	10×0.036= 0.36	2.9
N_2.....80	80×0.019= 1.52	12.1
	12.58	100.0

The change in the carbon dioxide from 10 per cent. of the gas sampled to 85 per cent. of the gases dissolved in water shows how serious are the errors which can arise in sampling. If the sampling tank originally filled with pure water should be only half emptied so that it would be half filled with gas of the above composition and half filled with water, and then it should be allowed to stand till equilibrium were attained, 7 per cent. of the gas would be dissolved by the water with the following result.

Original composition of gas, per cent.	Composition gas after standing over water, per cent.	Composition of gases dissolved by water, per cent.
CO_2.....10.0	5.2	73.4
O_2.....10.0	10.4	5.0
N_2.....80.0	84.4	21.6

The above illustration shows that in chimney gases it is not at all impossible to have an error of 50 per cent. in the CO_2 through carelessness in sampling. Errors of similar nature, although hardly of such large proportions, will arise with other gases. With illuminating gas it is the important class of illuminants of

the ethylene series which is most seriously affected. If it is worth while taking a sample at all it is worth while to saturate the water with which the gas is to come in contact.

7. Saturating Water in Sampling Tanks.—When the gas to be sampled is under pressure it may be bubbled through the water contained in a bottle, best only about two-thirds full of water and loosely stoppered. The air of the bottle will soon be replaced by the gas which will thus act on the constantly changing surface of the liquid as well as on the surface exposed to the bubbles. An occasional vigorous shake will greatly accelerate absorption. Under these conditions the water will become practically saturated in fifteen minutes. It is not wise to attempt to saturate water by bubbling the gas through it while in an open beaker, since the constant presence of the air above the liquid defeats the very object aimed at.

The water in tanks of the form shown in Fig. 2 may be readily saturated if suction is available by connecting tank 1 to the gas main as shown and connecting the suction pipe to cock E. The gases will then bubble through the water and pass out E. Where suction is not available the procedure is as follows. Start with tank 1 full of water and tank 2 empty. Fill tank 1 with gas and connect the cocks E on the two tanks with rubber tubing. Raise tank 2. Water will flow from 2 into 1 and gas from 1 to 2. When each is approximately half-full close the valves and shake. Finish passing the water from 2 into 1 and disconnect the rubber tube from E of tank 2. Draw a fresh tankful of gas into 1, allowing that in 2 to escape into the air. Connect the cocks E with rubber tubes as before and repeat the process of dividing the gas and water between the two tanks and shaking. After three such operations the water will be sufficiently saturated.

8. Collecting an Average Sample Representative of a Definite Period.—It is frequently desirable to determine the average composition of gases flowing through a flue for a period of time which may be 15 minutes or 24 hours. If the period is not longer than an hour the use of two cu. ft. tanks as shown in Fig. 2 is satisfactory. A represents the multiple sampling tube projecting into a flue. B is a calcium chloride tube loosely packed with cotton or asbestos to filter out dust. C is a bubbling tube to indicate the rate of flow of the gas. The first step in a test is

to saturate the water of the tanks as previously directed. At the close of this operation tank 1 should be full of water and tank 2 of gas and the sampling tube and the filter should be full of gas. To commence the sampling operation D is opened fully and F is opened slightly until gas bubbles through C at the rate desired. It is a mistake to open widely the lower stopcock on the sampling tank and control the flow of gas by partially closing the upper stopcock, since with this procedure the gas in the tank is under

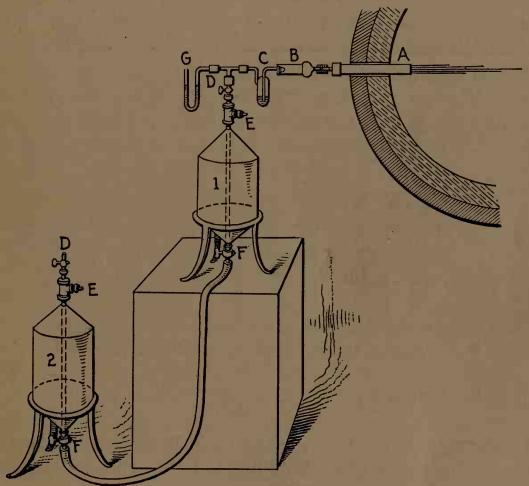

FIG. 2.—Apparatus for aspirating a sample of gas from a flue.

an unnecessarily reduced pressure and there is an unnecessary risk of leakage. The gas in tank 2 escapes through the open cock at the top. The pressure gage at G will indicate if the sampling tube or the filter becomes choked. The rate of gas flow should be so adjusted that tank 1 will be almost filled with gas at the end of the period. There should still remain enough water to act as a stirrer for the gas when the tank is shaken vigorously to mix the contents. This mixing is a simple precaution which should never be omitted. It is true that gases do

mix by diffusion but the rate is a slow one and it is never safe to rely on diffusion to give a fair sample. After the gas in tank 1 is mixed a portion may be transferred through cock E to a laboratory gas holder for analysis. To get ready for the next sample the E cocks on both tanks should again be connected by the rubber tube and the gas transferred to tank 2 so that the water in tank 2 will remain saturated.

If the sampling period is to extend for much more than an hour the flow of gas through the sampling tube becomes so slow that a multiple sampling tube is not to be relied on. The use of the additional apparatus shown in Fig. 3 remedies the difficulty where a continuous aspirator is available to draw a rapid stream of gas through the sampling tube. The gas filter, bubbling tube and sampling tanks of Fig. 2 are to be attached to cock A of Fig. 3. The sampling tanks may then be set to take as slowly

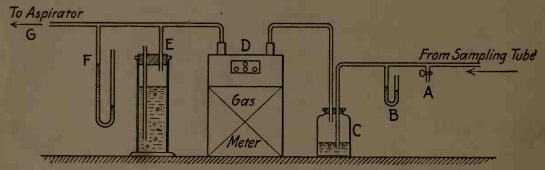

FIG. 3.—Continuous gas sampling apparatus.

as may be desired a portion of the representative rapidly flowing gas stream.

In Fig. 3, B is a pressure gage to indicate any obstruction of the sampling tubes, C is a bubbling bottle to give a visual control of the rate of the stream, D is a gas meter which may be omitted if not needed, E is a pressure control and F a pressure gage on the line from the aspirator. The suction on the sampling tube as shown by gage B should be only a few tenths of an inch of water. It is difficult, however, to get an aspirator to work properly when nearly shut off so that the aspirator is opened enough to work efficiently and the suction on the line is kept down by the regulator E. The suction on B may be regulated by the depth to which the tube in E is immersed.

The title of this section calls for the collection of a sample representative of a definite period. The foregoing procedure

only accomplishes it approximately. In order that the sample should be truly representative a given proportion, say one-tenth of 1 per cent. of the gas, should be constantly passing through the sampling tube. If the flow of gas in the main dropped to one-third of its former rate, the flow of gas through the sampling tube and into the sampling tank should also decrease. The ideal to be striven for is to have in the small sampling tank gas of the identical composition that there would be in a large gas holder where all of the main gas stream had been gathered and mixed. This can only be accomplished by a sampler which takes representative quantities as well as qualities of gas. The sampling apparatus described is supposed to work at a constant and not a proportionate rate, but it does not even do this accurately. It is not, however, possible to take a truly proportional sample without great elaboration of equipment and the method described is usually sufficient.

9. Collecting a Representative Instantaneous Sample.—The problem of a representative instantaneous sample is in some ways simpler than that involved in collecting a sample to represent a longer period. If the apparatus shown in Fig. 3 is attached to a multiple sampling tube a sample drawn at A should be fairly representative. If desired an Orsat burette or similar apparatus may be attached permanently at A.

10. Storing Gas Samples.—Samples of gas obtained as directed in the preceding section are too large for ready transportation to the laboratory for analysis. It is usually convenient to transfer a portion to a small glass gas holder which is advantageously of the type proposed many years ago by Hempel and shown in Fig. 4. This consists of a bulb terminated above by the gas inlet of capillary tubing bent in the form of a U to allow a water seal and at the bottom by a larger tube for the water supply. The transfer of gas is accomplished in the following stages. Attach at cock E of Figs. 2 and 4 a glass tee carrying at A a rubber connection and a small funnel and at B a rubber connection. Fill the gas holder with water taken from the large sampling tank 2 of Fig. 2, which is saturated with the gas, and connect the gas holder at B as shown in Fig. 4, with the exception of the screw clamps at A and B. Open valve E and blow gas through the tee and out A to expel air. Close E and force water

from the small gas holder into the funnel. Tighten clamp A. Fill the glass gas holder nearly full of gas and close E. Open A cautiously and allow water to flow from the funnel and fill the capillary seal of the gas holder. Close clamp B and disconnect the gas holder from the tee. Elevate the levelling bottle so as to put the gas in the holder under slight pressure, and close the clamp C at the bottom of the holder. The gas is now stored in a

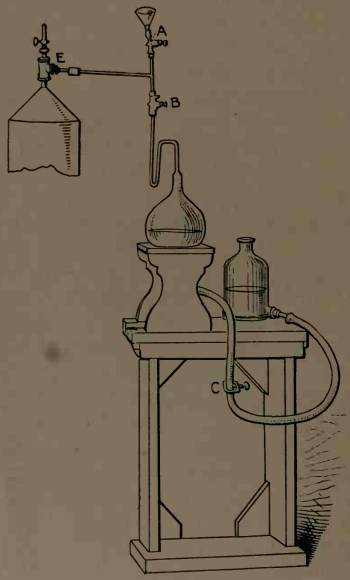

FIG. 4.—Glass gas holder for storing samples.

glass vessel closed at the top by a capillary tube filled with water, which in turn is closed by a clamped rubber tube at the top of the capillary. At the bottom the holder is similarly closed by a column of water. The gas is thus in contact with nothing but glass and water and if the latter has been previously saturated, may be preserved without change for months. The above form of gas holder is always reliable.

Gas holders of the floating type are not to be relied upon for there is always diffusion of gases through the water, and after several hours evident changes may be found. There are numerous forms of gas holders where stopcocks are relied upon to prevent leakage. Stopcocks may be tight or they may not and anyone who has had experience with the irritating doubts attendant upon their use will prefer not to trust them more than is necessary. The same thing holds true of rubber stoppers and connections. Gases may, however, be transported quite safely in glass bottles with rubber stoppers provided a little water is left in the bottle and the stopper is wired tightly in and covered thickly with paraffine. The bottle is then to be kept upside down. Under these conditions the small amount of water in the bottle forms a seal on the inside and the paraffine a seal on the outside, re-enforcing the rubber. When samples of this sort are to be shipped by express they should be packed in crates without a top so that care will always be taken to keep the proper end up. Where gases have to be stored a long time and especially where they must be shipped, the truly safe way is to collect them in glass tubes drawn out at each end and fuse the ends in a blowpipe flame.

CHAPTER II

GENERAL METHODS OF TECHNICAL GAS ANALYSIS

1. Introduction.—Gas analysis is an extremely useful method for controlling the operation and checking the efficiency of many industrial operations. All of the manifold industries using fuel as a source of heat and almost all industries engaged in producing fuel or utilizing it in any way find in gas analysis a valuable assistant. There are very many special industries which require the analysis of gases which are peculiar to themselves and not connected with fuels, but though the general methods of gas analysis here given will often apply to these cases, no attempt will be made to develop those applications which might better be taken up in connection with a study of the particular industries. This chapter will consider only the gases arising from the utilization of fuels.

The purpose for which the analysis is desired will influence the methods to be employed and the kind of apparatus to be used, for time consumed and liability to errors increase rapidly with the number of constituents to be determined. The analysis is to be made as simply as possible, small percentages of gases unimportant for the purpose of the analysis being neglected and groups of related gases being frequently determined together. In boiler firing and in the operation of all furnaces heated by combustion of fuel, the variations in the percentages of carbon dioxide, oxygen and carbon monoxide show at once the changes in efficiency of the furnace. In the operation of gas producers these three constituents with the added determination of hydrocarbons and of hydrogen suffice for most purposes. When gas is to be sold to consumers, as is the case with a city gas supply, a more complete analysis is often necessary and not infrequently some uncommon and minute constituents must be sought as an explanation of trouble.

This adaptation of the means to the end is a characteristic of technical analysis, which seeks only the particular information

of value for the purpose in hand. On this account gases from different sources will be considered separately, although there may be much in common between them. There are various operations common to almost all processes of gas analysis which may well be considered before passing to special cases, and such general considerations form the subject of this chapter.

2. General Method.—The method preferably followed in technical gas analysis requires a measurement of the initial volume of the mixed gas, the absorption of a single constituent by an appropriate reagent, and the measurement of the new volume, the constituent absorbed being determined by difference. Where no suitable absorbent is known for a given constituent it is desirable to transform the gas into some more suitable compound. It is necessary in order that these changes in volume due to absorption be correctly noted, that the temperature and pressure of the gas be known at each step, and it would be ideal if both the temperatures and pressures could be kept absolutely constant throughout the process. This can never be accomplished, although by special apparatus described in Chapter VI on Exact Gas Analysis errors due to change in external temperature and pressure during an analysis may be automatically eliminated. This procedure is, however, more complicated than is necessary for technical work where it is usually sufficiently accurate to make the assumption that the temperature of a water-jacketed burette in a laboratory does not vary during the hour that may be required for an analysis, and that the barometric pressure does not change in the same period. Since this simpler procedure is sufficiently accurate for most technical purposes, it will be described first. The historical development of the present apparatus and methods is discussed in Chapter VI on Exact Gas Analysis.

3. The Gas Burette.—The gas burette has its zero point at the top and is usually of 100 c.c. capacity. It is closed at the top by a stopcock or sometimes simply by a rubber tube and a pinchcock and should always be enclosed in a water jacket. Almost all forms of gas burettes will answer the above description, but there are many differences of detail, the most important being the style of the stopcock which closes the burette at the top. The form of apparatus which has been evolved in

the laboratory of the University of Michigan[1] and which has given good service during the past ten years is shown in Fig. 5, which illustrates the apparatus as it appears in service. Details are given in Fig. 6. The burette-stand may be improvised from an ordinary iron stand, one of whose rings of external diameter slightly greater than the water jacket of the burette has been provided with a brass collar, thus making a

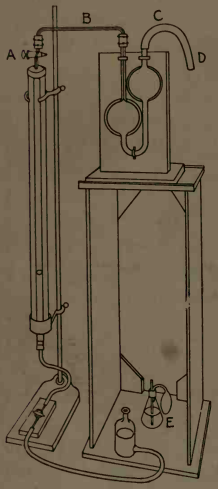

FIG. 5.—Gas burette and pipette.

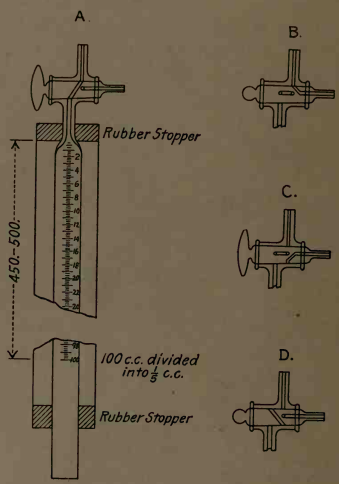

FIG. 6.—Details of gas burette.

cup in which the rubber stopper of the water jacket rests without binding. Another ring large enough to slip loosely over the water jacket serves to keep the burette vertical. A segment is sawed out of the front of this ring to allow an uninterrupted view of the graduations, and it is wrapped with chamois skin until it fits as snugly as desired. A spring clamp made from sheet brass makes a more elegant upper support. By this simple arrangement the burette may be raised, lowered, or swung to

[1] White and Campbell, *J. Am. Chem. Soc.*, 27, 734 (1905).

one side at the convenience of the operator, and may be tipped in any position while carrying, without danger of breakage.

By reference to A of Fig. 6 it will be seen that the body of the burette is a perfectly straight tube. It is closed at the bottom by a one-hole rubber stopper, which need not even be wired in, unless the burette is to be filled with mercury. To clean the burette, all that is necessary is to take out the rubber stopper and lift the burette and its jacket out of the rings when it may be turned upside down, swabbed out as an ordinary burette, and then swabbed with a clean dry muslin which is more efficient than a wet cloth in removing the film of grease which causes the drops to hang to the glass. Caustic soda may be used or chromic acid, but they are not usually necessary.

4. Care of Stopcock.—The stopcock of a gas burette is very carefully ground and polished so as to be as nearly gas tight as possible. Particles of grit getting into the capillary opening are apt to cut a groove around the stopcock so the opening is bored diagonally in order that the grooves worn in this manner may be parallel and non-connecting. This device is of assistance but the stopcock must still be handled carefully.

To keep in good condition remove the stopcock from the burette, wipe it off with a dry cloth and see that the capillary openings are clean. Do the same with the seat into which it fits in the burette and the capillaries with which it connects. Rub a thin coat of some lubricant over the stopcock. Vaseline is inferior. A material made by melting one part of best black rubber at as low a temperature as possible and stirring into it one part of paraffine and one part of vaseline answers well when it is carefully made. The author has found anhydrous lanolin the best material. The lubricated stopcock should be pressed gently into the dried seat and turned a couple of times, when the space between the stopcock and the seat should appear perfectly translucent without air bubbles or any discontinuity. If too much lubricant is used it will work itself into the capillaries and clog them. If either the stopcock or the seat is wet the lubricant will not adhere well. These stopcocks are expensive and it is advisable to fasten them to the burette with a fine copper wire attached to the stopcock so loosely that it can turn readily. It is not advisable to use a rubber band for this

purpose since it sticks to the handle of the stopcock and exerts a torsion sufficient sometimes to turn the cock at an inopportune time. The stopcock should always be loosened in its seat when the burette is to be put away and it is admirable policy to always clean it and make it ready for use again before setting it aside.

5. Saturating the Water of the Burette.—The liquid filling the burette is almost always water which allows much more rapid and convenient and in some ways more accurate manipulation than mercury does. It should be saturated with gas similar to that which is to be analyzed. If the gas is air this precaution may often be omitted, since distilled water is usually saturated with air. The precaution should not be omitted with other gases, especially those like flue gases rich in the more soluble carbon dioxide. The errors due to solubility of gases are discussed more fully in Section 6 of Chapter I. Place 200 c.c. of water in a flask or bottle of about 400 c.c. capacity and lead in a stream of gas through a glass tube passing through a loosely fitting cork, shaking occasionally. If the supply of gas is limited a smaller flask may be used and the loose cork may be pressed down tight after the air has been displaced. Shaking the flask facilitates absorption. It is not necessary that the water be absolutely saturated and five minutes is usually ample time for the operation.

6. Drawing the Sample of Gas into the Burette.—The gas to be analyzed is assumed to be contained in a gas holder of a type similar to that shown in Fig. 4 of Chapter I, but the directions for use of this type of gas holder may readily be adapted to other types.

The tubing to connect the burette and gas holder should be capillary so that the air contained in it may be completely swept out without wasting much gas. A tube of 1 mm. internal diameter answers well. It should not be rubber because rubber absorbs heavy hydrocarbons from gases rich in these bodies and gives them back again to gases containing them in but small amount. It is necessary to make one rubber connection at each end of the capillary tube but the surface of rubber exposed to the action of the gases should be reduced to a minimum by bringing the ends of the glass capillary tubes into direct

contact with each other, or, if it is necessary to leave a pinch-cock on the rubber, as close to each other as possible. The glass tubes should be cut off square and the sharp edges softened in a flame sufficiently to prevent the cutting of the rubber but not enough to constrict the capillary opening of the glass tube. The rubber tube should fit tightly to the glass and be of the best quality black gum rubber, free from any internal ridge where the seam has been joined. The inside of the rubber tube may be moistened with water or preferably with glycerine to make it slip more readily over the glass. The rubber connections to the capillary should be bound with wire as a further safeguard against leakage. Soft copper wire of about 22 B. & S. gage is suitable. Finer wire is too apt to cut the rubber. Heavier wire is apt not to pull up snugly. Copper wire of 24 B. & S. gage insulated with cotton and paraffined like that used for annunciators, is the best material as it is strong enough and does not cut the rubber. It is a mistake to wrap the wire several times around the tube. A piece of wire about 2 in. long should be wrapped once around the tube. The crossed ends are then to be grasped close to the rubber with a pair of pliers and tightened with a single half turn of the wrist.

No rubber joint can be relied on to be gas-tight for a long period of time. A joint prepared as directed here should, however, not allow any perceptible leakage in the course of a gas analysis although it is wiser not to subject it to any higher gas pressure or suction than necessary.

The method of connecting the gas holder and the burette is shown in Fig. 7 where A is the gas holder, D, a bent capillary tee tube and F the gas burette. Before making the connections the gas burette is to be filled with saturated water and the cock closed by a turn of 180° which completely seals both the capillaries below and above the cock. The capillary tee tube is to be inserted into the open rubber tube above the clamp B, connected at E as shown and the joints are to be wired. The gas in the holder is to be put under pressure by raising the levelling bottle and clamp B opened. Cock C is then opened slightly until the water in the capillary of the gas holder rises to displace all the air in the funnel arm. Cock C is then closed and cock F turned 90 degrees to the position shown in Fig. 7 and at B in

Fig. 6. The rest of the water in the capillary A moves through D and out F driving all air ahead of it. Some gas may also blow out if the manipulator is not skilful, but this does no harm. Cock F is then turned 90 degrees opening the passage to the burette as shown at A in Fig. 6 and the gas passes into the burette. When enough gas is in the burette another 90-

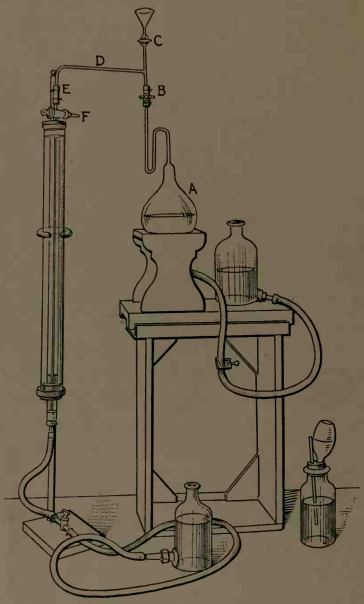

Fig. 7.—Gas burette and gas holder.

degree turn of the cock in the same direction to the position C of Fig. 6 stops the gas flow. A few cubic centimeters of water are placed in the funnel above C (Fig. 7), the pressure in the gas holder is changed to suction, cock C is opened and water flows into the capillary of the gas holder re-establishing the seal. The clamp B may then be closed and the capillary disconnected. This procedure allows transfer of the gas without

possibility of change in composition and restores the seal of the gas holder at the close of the operation. Instead of the tee with cock and funnel blown as one piece the simpler apparatus shown in Fig. 4 of Chapter I may be used.

7. Measuring a Gas Volume.—The volume of gas is to be measured at the temperature of the water jacket and at barometric pressure. The temperature of the gas as drawn into the burette does not ordinarily differ very many degrees from that of the jacket water but it should be allowed to stand a few moments to allow it to attain that temperature. During these minutes the gas if not already saturated with moisture rapidly absorbs it from the moist burette walls and becomes saturated as it should be before its volume is measured.

Delay in reading the volume is also necessary to allow the film of water which adheres to the burette walls as the sample is rapidly drawn in, to run down. If the walls of the burette are clean the water will have run down in three minutes so completely that the volume has become approximately constant. If this precaution is neglected the volume read may easily be in error by 0.2 c.c., even with a clean burette. Some operators object to this three-minutes wait as too great hindrance to rapid work and it is true that if the readings are made by a skillful operator immediately after the introduction of the gas, the errors of successive readings are almost constant and disappear in the subtractions. If, however, the practice is followed of detaching the used pipette and connecting the new one before reading the volume of gas, sufficient time will have elapsed without the operator's having been idle.

To obtain a sample of exactly 100 c.c. a sample of slightly more than 100 c.c. is initially taken and compressed by raising the levelling bottle until the bottom of the meniscus is exactly opposite the 100 c.c. mark. The stopcock at the bottom of the burette is then closed so that the mensicus cannot change its position and the stopcock at the top of the burette opened momentarily to the air, to allow the pressure in the burette to equalize itself with the outside air. The volume of gas should now be 100 c.c. at atmospheric pressure but the correctness of the volume should be checked by opening the stopcock connecting the levelling bottle with the burette and raising the levelling

bottle until its water surface is at the same height as that of the water in the burette. The connecting stopcock may now be closed and the volume read as indicated by the bottom of the meniscus. If the operation has been properly carried out the volume should be exactly 100 c.c. This volume is subject to correction for error in the burette and if an exact 100 c.c. sample is desired the meniscus may have to be set on some other figure than the 100 mark.

8. Calibration of a Gas Burette.—A gas burette may be calibrated like any other form of burette by wiring a one-hole rubber stopper carrying a stopcock into the bottom of the burette and weighing the water delivered. Burettes of good quality are usually calibrated accurately enough throughout their cylindrical portion to make this form of calibration unnecessary for technical work. The burette should, however, be calibrated in its upper portion, especially if its previous history is not definitely known, since its original stopcock may have been broken and the volume of the neck changed when a new stopcock was fused on, and since it may have been calibrated by the maker to be used when filled with mercury instead of with water. The error in this latter case arises from the custom of reading the mercury meniscus at the top of its convex surface and the water meniscus at the bottom of its concave surface. It will be readily seen that if the mercury meniscus stands at 10 c.c. there will be more gas in the burette than if the same burette is filled with water with the bottom of its meniscus at 10 c.c. This error may amount to 0.2 c.c. in an ordinary burette. Both of these errors are constant ones throughout the cylindrical portion of the burette and independent of the volume of gas in the burette. It will therefore be sufficient to determine them once.

The most convenient method is to compare one burette with another. Draw into each burette about 10 c.c. of air, the exact amount being entirely immaterial. It is only necessary that the volume be large enough so that the reading is in the cylindrical portion of the burette. It is not desirable that the volume be large since the error caused by water adhering to the walls of the burette increases with the size of the sample. Connect the burettes by a bent capillary tube making the rubber connections while the stopcock of one of the burettes is

open to the air so that the air enclosed in the capillary will be under atmospheric pressure. Read the volume of the air in each burette at atmospheric pressure as usual. We will assume that Burette A which has an unknown constant error "x" is the one being tested and that Burette B is the one assumed to be correct throughout its cylindrical portion, although it may itself have a similar unknown constant error "y." Transfer all of the air from A to B stopping the water in A just at the stopcock and read the new volume in B. The notes will then read somewhat as follows:

CALIBRATION OF BURETTE A AGAINT BURETTE B

Burette A		B
Initial vol. air	10.6 c.c. $+x$	9.5 c.c. $+y$
Second reading	0	20.3 c.c. $+y$
Subtracting	10.6 c.c. $+x$	$=$ 10.8 c.c.
		$x = +0.2$. c.c.

This result translated into words means that there must be added to each reading of Burette A 0.2 c.c. Since the probable error of observation is 0.1 c.c. several successive determinations should be made and the mean taken.

It is always wiser to record this error in the notebook after each reading, 92.5+0.2, and not simply make the correction mentally and record 92.7, since there may always come a time when the analyst will be in doubt as to whether he has made the mental correction or forgotten to make it before recording. This error automatically disappears whenever one volume is subtracted from another and it is therefore only necessary to apply it when the absolute volume needs to be known as is the case with the initial volume taken for analysis. This makes the error vastly less important than it would be otherwise, for if in an analysis of flue gas an apparent 100 c.c. sample is taken which becomes when corrected 100.2 c.c., and 10 c.c. is found to be CO_2, the percentage of CO_2, neglecting the burette calibration, is found to be 10.00 per cent. and allowing for the calibration 9.98 per cent., which when rounded off becomes 10.0 per cent. as before. The case is different, however, when a sample of 10.0 c.c. is taken as is the case in explosion analysis. If the

analysis showed 8.0 c.c. of hydrogen, the percentage neglecting the calibration would be figured as 80.0 per cent. but allowing for the calibration would be 78.4 per cent. It is preferable to record the calibration correction even though it may be later neglected in the calculation.

9. Gas Pipettes.—The various gases are determined so far as possible by absorption in suitable reagents contained in pipettes of the form shown in A, B, and C of Fig. 8. The use of a separate pipette for each reagent was first brought into general use by Hempel. These pipettes differ from his in the elimination of the deep U bend in the capillary, which is retained only in the explosion pipette. This deep bend is a distinct disadvantage

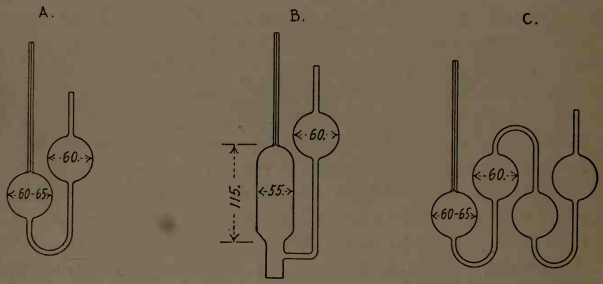

FIG. 8.—Details of gas pipettes.

since drops of reagent collect in it and are later carried into the burette. It is no longer needed when used with the burette just described. These pipettes are mounted on wooden stands, as shown in Fig. 5, which should be paraffined and not shellacked so that they may not be affected by reagents accidentally spilled.

10. Connecting the Burette and Pipette.—The greatest manipulative error with most forms of gas analysis apparatus comes from the frequent changes of pipettes necessary. Unless the operator is skilful there is danger of loss of gas or inclusion of air. The form of burette just described prevents this error. The general arrangement of the burette and pipette is shown in Fig. 5. The stopcock A is turned to the position shown at B in

Fig. 6, the bent capillary B whose dimensions are immaterial, is connected to the burette and pipette and the rubber joints are wired. The operator blows through the rubber tube (D of Fig. 5) on the last bulb of the pipette, forces the liquid from the pipette up the capillary and over to the stopcock, driving all the air ahead of it, and closes the stopcock by turning it 90° to the position D of Fig. 6. The capillary tube is now entirely full of liquid and the operator has only to compress the gas in the burette by raising the levelling bottle, and turn the stopcock a half turn to the proper position (A of Fig. 6) when the gas will pass into the pipette. By this method of manipulation, it is easy to transfer the gas from burette to pipette without loss or inclusion of air. Furthermore, since the volume of the capillary is entirely immaterial, it may be chosen of larger diameter than usual, permitting more rapid work and lowering the pressure necessary to force the gas through it rapidly. It has been found advantageous to have the stopcock left-handed, as indicated, so that the hand manipulating the stopcock may not interfere with a clear view of the meniscus of the liquid advancing along the capillary tube.

11. Details of a Simple Gas Analysis.—Accuracy in gas analysis is dependent on the exercise of very great care in manipulation. When the analysis is completed there is no way of going back over the ground again as may so frequently be done in ordinary chemical analysis, and it is not always possible to make duplicate analyses. The analyst must be able to state with confidence that every precaution was taken to ensure an accurate result. Detailed directions will be given for the analysis of a gas which may be assumed to be air. This is a very convenient material for practice since it may be obtained in unlimited quantities and of practically constant composition.

The burette is to be cleaned (§ 3), the stopcock lubricated (§ 4), and the water saturated (§ 5). Draw the sample of gas into the gas burette (§ 6), measure it (§ 7), and connect it to a pipette containing KOH (§ 10), for determination of CO_2. The connections having been properly made and the air driven out of the capillary tube as indicated, raise the levelling bottle and pass the gas into the absorbent, letting the water of the burette follow until it reaches the bottom of the capillary of

the pipette. The gas is now all in the pipette. Let it remain for about three minutes gently shaking the pipette occasionally to agitate the gases and cause more rapid absorption. When it is believed that absorption is complete pass 1 c.c. of the burette water into the pipette to rinse from the capillary any reagents which might have been splashed into it, and then draw back the gas into the burette, pulling the liquid of the pipette as far as the stopcock on the burette. By a quarter turn of the stopcock to position B of Fig. 6 the connection between the pipette and the burette is closed while that from the pipette to the air is open. This causes the reagent to siphon back into the pipette. After waiting for three minutes to allow the liquid to drain from the walls of the burette read the volume as before and report the decrease in volume as the volume of the CO_2 absorbed. There is no certainty that all the gas has been absorbed. The only way for the operator to be sure is to pass the gas back again into the pipette and repeat the operation until the volume remains constant. Disconnect the pipette from the capillary tube, and rinse out the capillary tube with the wash bottle shown at E of Fig. 5, thus completing the first step of the analysis. If the gas being analyzed is air, the volume after treatment with KOH should be the same as before since the volume of CO_2 in the air, 0.04 per cent., is too small to be measured with a burette of this type.

In the practice analysis of air the next determination would be that for oxygen which would be absorbed by phosphorus or alkaline pyrogallate as directed in §§ 3 and 4 of Chapter III. Air contains 20.9 per cent. of oxygen by volume. The residue is assumed to be nitrogen.

Successive analyses of similar gases may be made without changing the water in the burette provided that none of the reagents have been carelessly drawn into the burette. The greatest danger is from the caustic solution which will absorb some of the CO_2 from a newly introduced sample before its volume has been measured. Phenolphthalein in the water will show when it has become alkaline and should be changed. There is no objection to having the burette water faintly acid and there is the advantage that small amounts of alkali are neutralized and rendered harmless.

12. Accuracy of the Analysis.—Account should now be taken of the magnitude of various possible errors, some of which have not been mentioned. The smallest division on the burette is usually 0.2 c.c. and the volume may not with certainty be estimated by interpolation closer than 0.1 c.c. This probable error limits the accuracy of the process to 0.1 per cent. with a sample of 100 c.c. and an accuracy of 1.0 per cent. with a sample of 10 c.c. Change of temperature of the burette water during an analysis causes a change of 0.36 per cent. in the volume of the gas for each degree centigrade. Change of barometric pressure causes a change in volume of 0.13 per cent. for each millimeter of mercury change in pressure. There are other minor sources of error which will be mentioned in Chapter VI under "Exact Gas Analysis." It will be evident that it is perfectly useless to expect an accuracy of greater than 0.1 per cent. with apparatus of this type, and that an error of 0.2 per cent. is not improbable. An analyst who reports an analysis carried to hundredths of a per cent. only shows his own ignorance.

CHAPTER III

ABSORPTION METHODS FOR CARBON DIOXIDE, UNSATURATED HYDROCARBONS, OXYGEN, CARBON MONOXIDE AND HYDROGEN

1. Carbon Dioxide.—This gas is determined by absorption in a strong solution of either caustic soda or potash. Very concentrated solutions dry the gas and make it necessary to let it stand in the burette before reading the volume until it has again become saturated with moisture. Dilute solutions work too slowly. A solution of 50 grm. NaOH in 150 c.c. of water is recommended to be kept in the form of pipette shown in A of Fig. 8. The absorption is rapid, three minutes being always ample. The reaction may be accelerated by gently shaking the pipette or by passing the gas back and forth. Glass rods or perferably glass tubes are sometimes introduced into the pipettes to accelerate the absorption by offering a large wetted surface with which the gas may come in contact. If this device is used care must be taken that no gas bubbles are trapped in the pieces of glass tubing as may frequently be the case if they are less than 5 mm. internal diameter or if they do not stand vertically. If it is desired to place glass tubes in the pipette use the form shown in B of Fig. 8. It will be necessary to wire the rubber stopper firmly into place to prevent leakage of the caustic.

This reagent absorbs not only carbon dioxide but also sulphur dioxide, hydrogen sulphide and any other acid vapors which may be present. It may be used until almost all of the caustic has been changed to carbonate. One pipette will absorb about four liters of CO_2. There will be slow carbonate formation through exposure to the air but the reagent may be used without fear for several months provided it is used infrequently.

2. Unsaturated Hydrocarbons.—These gases are determined by absorption in a liquid which by addition forms saturated compounds from the unsaturated ones. In gases from coal the

predominating constituent is ethylene, C_2H_4, but smaller percentages of the other olefines are present and sometimes small amounts of acetylene, C_2H_2. A solution of bromine water made by diluting one volume of saturated bromine water with two volumes of water is the reagent preferred by the author. It is placed in the first bulb of the double pipette shown in C of Fig. 8, and the third bulb is filled with water to lessen the diffusion of bromine into the air of the laboratory. If the solution becomes bleached through formation of hydrobromic acid in the sunlight, it is sufficient to add a few drops of liquid bromine which again brings it up to its normal strength. It is unnecessary to have it so strong that the gas drawn back into the pipette shows pronounced yellow bromine fumes. When gases with more than a small per cent. of unsaturated hydrocarbons are brought into contact with bromine it is possible to observe the formation of the bromide as an oily film on the surface of the liquid. As this film retards reaction between the bromine and the gas, it is advisable to shake the pipette gently during absorption, when little drops of the heavier ethylene bromide may be seen falling to the bottom of the pipette. The gas drawn back into the burette will contain so much bromine vapor that its volume may even have increased in the process. It must be passed into a caustic solution and shaken for about one minute to remove the bromine fumes and then brought back into the burette and measured. The diminution in volume is to be reported as unsaturated hydrocarbons. A delicate test for the complete removal of these constituents is afforded when phosphorus is subsequently used as a reagent for oxygen. A fraction of a tenth of a per cent. of ethylene will completely prevent the reaction between phosphorus and oxygen. Three minutes shaking with the bromine is sufficient to remove the unsaturated hydrocarbons from most gases, but gases of high candle power, like Pintsch gas, sometimes require ten minutes. Treatment with bromine water should be repeated until phosphorus smokes when the gas is brought in contact with it.

Fuming sulphuric acid acts in the same way as does bromine water, but it is difficult to handle, attacks rubber tubing badly, and must be protected from the moisture of the air to avoid loss of efficiency.

3. Oxygen by Phosphorus.—Yellow phosphorus is an extremely reliable reagent for the absorption of oxygen when used under proper conditions. It combines with oxygen producing solid oxides of phosphorus and reacts with almost no other gases which might be present. The disadvantage attending its use is the danger of the reaction not taking place at all because of the presence of inhibiting catalyzers, because of too low temperature or because of too high a concentration of oxygen in the gas. There is, however, easy ocular evidence of the reaction so that there need be no uncertainty as to whether the reaction has taken place. When once started it goes to completion.

The pipette is of the form shown in B of Fig. 8. To prepare it for use the pipette is inverted and filled with water and into it are dropped sticks of phosphorus about 5 mm. in diameter which have been cut to proper length under water. The sticks are to stand vertically and fill the pipette practically full. The only advantage of the small sticks lies in their greater surface and in the convenience with which the pipette may be filled. It is possible to prepare them in the laboratory by melting phosphorus under water at a temperature a little above 44° C. and sucking it into a slightly conical glass tube. With expert manipulation this tube may be lifted from the warm water and plunged into cold water where the phosphorus will soldify and contract so that the stick may be pushed from the tube. It is simpler though not so elegant to mould the sticks in a tin dish about 5 in. long made with a corrugated bottom and provided with a rim about an inch high and a handle. This mould is submerged in a dish of warm water and enough phosphorus melted in it to fill the corrugations. It is then lifted out and placed in cold water till the sticks become solid. Molten phosphorus catches fire instantly in the air and produces dangerous burns on the skin. Particles of solid phosphorus dropped in cracks of a wet table or floor have been known to smoulder twenty-four hours and finally burst into flame. Great care must always be exercised in handling phosphorus and it is usually preferable to buy it already cast in small sticks. The pipette should be kept in the dark when not in use to avoid the deterioration of the phosphorus. Pipettes made from brown glass

retard the action of the sunlight. With proper care a phosphorus pipette should last for years without refilling.

When a gas containing oxygen is introduced into a phosphorus pipette there normally appears at once a dense white cloud of oxides of phosphorus which are evident even when the amount of oxygen is less than 0.1 per cent. of the total volume. All technical gases will contain this much oxygen, for even if they did not contain it originally they will have absorbed it from the water of the sampling apparatus or of the burette, so that the presence of these clouds is a sure indication that the reaction is progressing properly. Conversely the absence of any smoke means not that there is no oxygen present, but that there is something preventing the reaction. The reaction between oxygen and phosphorus is also attended by a glow, visible only in the dark, which disappears with the completion of the reaction. The white cloud consists of solid particles of phosphoric oxides which slowly settle and dissolve in the water. It is not necessary to wait for this, however, before drawing the gas back into the burette and measuring the oxygen absorbed for the particles possess very slight vapor tension and do not occupy an appreciable volume. The reaction should with certainty be completed in three minutes if the white smoke appears promptly and if the surface of phosphorus exposed is large. It will not accelerate the reaction to shake the pipette since the reagent is a solid and the pipette is so closely filled with sticks that diffusion will soon bring the oxygen to the surface of the phosphorus.

The sticks of phosphorus at first yellow and waxy become covered with a reddish crust on long exposure to light and are inactive. Such sticks may be melted under water, skimmed, and cast into new sticks. The inactive crust may also be removed by placing in the pipette a 10 per cent. solution of $K_2Cr_2O_7$ made faintly acid with H_2SO_4. The chromate becomes reduced to the green chromic salt with oxidation of the surface of the phosphorus. It is preferable, however, to avoid deterioration by keeping the pipette in the dark when it is not in use.

If the white vapors do not appear promptly when the gas is passed into the pipette, the explanation may be sought in four directions.

a. The temperature may be too low. It should be above 15° C.

b. The concentration of the oxygen may be too high. Moist phosphorus does not react at all with perfectly pure oxygen at ordinary room temperature. If the partial pressure of the oxygen is diminished either mechanically by an air pump or by dilution with an inert gas the reaction commences. With 50 per cent. oxygen it is violent, flame being produced and the phosphorus melting. There is danger of breaking the pipette. When the concentration is less than 30 per cent. the reaction proceeds quietly and the phosphorus does not melt.

c. An inhibiting catalyzer may be present. The most commonly occurring catalyzer is ethylene, a few hundredths of a per cent. of which completely prevents the reaction between phosphorus and oxygen. Acetylene, benzine, ether, hydrogen sulphide and many other substances possess similar though usually weaker powers. Fortunately they are practically all removed either mechanically or chemically by bromine water followed by caustic potash and the gas should always be thus treated if the white fumes fail to appear promptly.

d. The phosphorus may have been rendered inactive by a heavy dose of a catalyzer. It may be restored by replacing the water in the pipette with fresh water and passing several successive samples of air into the pipette until the phosphorus again smokes freely.

Commercial compressed oxygen should be diluted with nitrogen before analysis. The nitrogen may be conveniently prepared from air by passing a buretteful of air into the phosphorus pipette, disconnecting the pipette and closing it with a pinchcock. Twenty-five to thirty cubic centimeters of the oxygen are then to be drawn into the burette (note that a calibration error of 0.3 c.c. means 1 per cent. here) and the phosphorus pipette reconnected. There will be sufficient nitrogen in it to flush out the capillary connecting tube and fill the burette as well. The oxygen may now be absorbed by phosphorus. It is desirable to introduce the oxygen into the burette before the nitrogen which thus fills the upper part of the burette and comes in contact first with the phosphorus. If the reverse procedure were followed and the oxygen introduced in the burette last, it might be brought in concentrated form in contact with the phosphorus

and cause violent combustion, a trouble which the above scheme of procedure avoids.

4. Oxygen by Alkaline Pyrogallate.—This reagent is very frequently used, especially in apparatus of the Bunte or Orsat type. When used with proper precautions it gives accurate results. Pyrogallol is a trihydric phenol $C_6H_3(OH)_3$ which in alkaline solution is a strong reducing agent, becoming itself oxidized to other products. Unfortunately, unless the solution is freshly prepared and strongly alkaline there is danger of carbon monoxide being evolved as oxygen is absorbed. This not only causes the oxygen to be reported low, but also makes the carbon monoxide high. Berthelot has shown that a reagent made by taking a solution of 1 part of pyrogallol in three of water and mixing it with its own volume of a solution of 1 part of KOH in two of water will, when freshly prepared, absorb ten times its volume of oxygen without giving back more than a trace of CO, but that solutions which have been used too long or do not contain enough alkali may give up as much as 5 per cent. of the volume of oxygen absorbed as carbon monoxide.

The reagent should be kept in a double pipette (C of Fig. 8), the third bulb being filled with water to prevent action of the air on the reagent. It may also be kept in a single pipette (A of Fig. 8) provided a rubber balloon is fastened to the second bulb for the same purpose. The reagent works very slowly at temperatures below 15° C. Carbon dioxide and other gases which would be absorbed by alkali must be removed before testing for oxygen with pyrogallate.

Mr. H. A. Small in the author's laboratory tested the behavior of a solution of pyrogallate made up according to Berthelot's directions and kept in an ordinary four bulb pipette without any special precautions to prevent diffusion of oxygen into the pipette. Duplicate samples of air were analyzed almost daily for more than a month. During the first four weeks the reagent absorbed the proper percentage of oxygen although it was frequently necessary to shake more than three minutes to accomplish this. The 150 c.c. of reagent in the pipette had up to this time absorbed 1140 c.c. of oxygen. After this the absorption of oxygen became incomplete, the line of demarcation being quite sharp and the apparent oxygen of the air drop-

ping from 20.7 per cent. to 20.4 per cent. Tests showed that the oxygen was still being quantitatively absorbed but that about 0.3 per cent. of carbon monoxide was being evolved. These results confirm Berthelot's statements. According to our results 1 c.c. of the reagent absorbs 8.0 c.c. of oxygen. In case of doubt concerning the reagent it should be tested on air and should be rejected unless it absorbs 20.6 to 20.8 per cent. of oxygen.

5. Other Reagents for Oxygen.—Sodium hydrosulfite has been recommended by Franzen[1] as a cheaper and better reagent than pyrogallol. The solution is prepared by dissolving 50 grm. $Na_2S_2O_4$ in 250 c.c. H_2O and mixing this with 40 c.c. of a caustic solution made by dissolving 500 grm. NaOH in 700 c.c. H_2O. Each cubic centimeter of this reagent absorbs 10.7 c.c. oxygen. The equation for the reaction is as follows:

$$Na_2S_2O_4 + H_2O + O = 2NaHSO_3$$

The solution is placed in a pipette containing rolls of iron gauze to increase the absorbing surface. Franzen states that the absorption is complete in five minutes without shaking and proceeds almost as rapidly at 4° C. as at room temperature. There is no danger of the formation of CO in the process which constitutes the greatest objection to pyrogallate. An ammoniacal copper solution was proposed by Orsat[2] as a reagent for the absorption of oxygen. He used a cold saturated solution of ammonia and ammonium chloride in contact with metallic copper. Oxygen is readily absorbed and the liquid assumes a blue tint. He also called attention to the limitation in the use of this reagent caused by the action of the ammoniacal copper salt on carbon monoxide.

Oxygen may be accurately estimated by explosion with excess of hydrogen or by combustion with copper and these methods will be discussed later.

6. Carbon Monoxide.—The methods for absorption of CO are less satisfactory than for any of the other commonly occurring gases. The usual reagent is cuprous chloride Cu_2Cl_2 which on account of its slight solubility in water must be used either in acid or ammoniacal solution. The acid solution consists of a

[1] *Chem.-Berichte*, 39, 2069 (1906).

[2] *Annales des Mines*, 1875, 490.

practically saturated solution of cuprous chloride in hydrochloric acid of specific gravity of approximately 1.12. Since the acid is only a solvent, its exact concentration is immaterial. Commercial acid may be used. About 150 grm. of the cuprous chloride will dissolve in a liter of acid of this concentration. This solution of cuprous chloride when pure is perfectly colorless but it darkens through slight oxidation as on exposure to the air, so that the usual solutions are black. It is possible to keep it colorless by placing in the reagent bottle or in the pipette copper turnings or copper wire, but it does not increase the efficiency of the reagent. If the oxidation proceeds so far that the solution becomes green, due to complete oxidation to the cupric state, the solution is worthless until it is again reduced to the cuprous state.

The reagent is kept in a double pipette whose third bulb is filled with HCl of sp. gr. 1.12 instead of water so that in case the cuprous chloride spills into it, it will not be precipitated. The gas which must have been previously freed from unsaturated hydrocarbons and oxygen is passed into the pipette and shaken for three minutes, then drawn back to the burette and passed into a second pipette containing fresh cuprous chloride where it is again shaken for three minutes, drawn back and measured. The HCl vapors in the gas may be neglected. There is no method of knowing whether the absorption of the CO has been complete. The only safe way is to repeat the absorption using a fresh solution until the volume becomes constant. Usually two absorptions of three minutes each are sufficient.

The reaction between carbon monoxide and cuprous chloride has not been definitely worked out. Jones[1] has shown that under certain circumstances a crystalline compound of definite composition results—Cu_2Cl_2, 2CO. $4H_2O$. In the dilute solutions present in gas analysis, however, the reagent behaves exactly as if it dissolved the carbon monoxide. When a perfectly new solution is used the CO will be practically completely removed. As the CO in solution increases there comes apparently an equilibrium between that in the gas and that in the solution, with the result that the absorption is incomplete. If a gas with only a small amount of CO is brought in contact

[1] *Am. Chem. Jour.*, 22, 287.

with a solution which has absorbed much, the gas will increase in volume due to CO given up by the solution. Each cuprous chloride pipette should bear a label on which should be recorded the number of cubic centimeters of carbon monoxide which has been absorbed. When it has absorbed more than 10 c.c. it is not safe to rely on the results. In practice the analyst should have two pipettes for cuprous chloride, one, which has absorbed considerable carbon monoxide, to be used first, and another, which should be kept almost entirely fresh to follow the other. When this second pipette has absorbed 10 c.c. of CO it should be used as the first pipette and the former first pipette should be emptied and refilled with fresh reagent. The solution may be regenerated if desired by boiling it for half an hour in a flask containing some metallic copper and provided with a reflux condensor to prevent much loss of acid. The feebly held CO is driven off by the boiling and any oxidized solution is reduced to the cuprous state again.

The ammoniacal solution is made by suspending about 150 grm. of cuprous chloride in a liter of distilled water into which ammonia gas is passed until the liquid becomes a pale blue color. The ammoniacal solution slowly regenerates itself on standing, the CO becoming oxidized to $(NH_4)_2CO_3$ and a mirror of metallic copper depositing. The NH_3 gas must be removed by an acid pipette before the correct amount of CO absorbed may be read.

Carbon monoxide may be estimated by explosion or combustion as described in the next chapter. Minute amounts of it may be estimated by the I_2O_5 method given in Chapter VI on "Exact Gas Analysis."

7. Absorption of Hydrogen.—Hydrogen may be absorbed by palladium sponge superficially oxidized to palladous oxide, according to the method of Hempel. It is necessary to regenerate the palladium after each experiment and the reaction is prevented by small amounts of carbon monoxide, hydrochloric acid and other constituents so that it is not a method which has found much favor.

A solution of palladous chloride as prepared by Campbell and Hart[1] is a better reagent. It is used as an almost neutral 1 per cent. solution prepared by dissolving 5 grm. palladium wire in

[1] *Am. Chem. Jour.*, 18, 294 (1896).

30 c.c of HCl to which is added 1 or 2 c.c. HNO_3. The solution thus prepared is evaporated just to dryness on the water bath, redissolved in 5 c.c. of HCl (sp. gr. 1.20) and 25 or 30 c.c. of water, warmed till solution is complete and diluted to 750 c.c. It is placed in a simple Hempel pipette made to be readily detachable from its frame so that the bulbs may be placed in a water bath. The first bulb of the pipette should have a capacity of at least 150 c.c. to allow for expansion of the gas and water vapor when the solution is warmed. The gas freed by the usual methods from CO_2, C_nH_{2n}, O_2 and CO, and containing H_2, CH_4 and N_2 is passed into the pipette and the water from the burette passed over to seal the capillary of the pipette. A screw clamp is placed on the rubber connecting tube and the pipette disconnected from the burette and placed in a water bath at 50° C. for an hour and a half. A higher temperature does no harm provided it does not expand the gas so much as to cause it to bubble out of the first bulb or to leave only a small amount of reagent in contact with the gas in the first bulb. The hydrogen reacts with the palladium chloride forming metallic palladium and HCl. The total decrease in volume is reported as hydrogen. The reagent may be counted on to absorb one-third of its volume of hydrogen completely in an hour and a half. Larger quantities will be absorbed more slowly. It is readily regenerated by rinsing from the pipette, evaporating just to dryness on the water bath, dissolving in 5 or 6 c.c. HCl and 4 or 5 drops of HNO_3 and again evaporating. The dry palladous chloride is dissolved by adding 2 c.c. conc. HCl and a small amount of water and is then diluted to its original volume. The method is accurate and satisfactory. Carbon monoxide and other reducing gases behave like hydrogen and must be removed previous to the test but hydrocarbons of the methane series are not affected. The chief objection to the method lies in the time consumed which makes it frequently necessary to correct the gas volumes for change in room temperature and barometric pressure. A memorandum should be made of the temperature of the burette jacket and of the barometric pressure before and after the test and corrections made if necessary.

Paal and Hartmann[1] recommend a solution of colloidal

[1] *Chem. Berichte*, 43, 243 (1910).

palladium made by dissolving 2.44 grm. collodial palladium manufactured according to Paal's process by Kalle (= 1.5 grm. palladium) and 2.74 grm. of sodium picrate in enough water to bring the volume to 130 c.c. Gaseous hydrogen dissolves in the aqueous palladium solution and reduces the picric acid. Hempel[1] has made a critical study of this method and reports that a solution prepared in this manner will absorb in 15 minutes

when freshly prepared	21.2 c.c. H_2 per 1 c.c. reagent.
after 79 days	16.2 c.c. H_2 per 1 c.c. reagent.
after 1 year	1.6 c.c. H_2 per 1 c.c. reagent.

He states that a fresh solution may be safely trusted to absorb completely 7.2 c.c. H_2 per centimeter reagent in three minutes if heated to the temperature of the blood. He advocates the preparation of the solution in small quantities and its use in a pipette filled mainly with mercury. A disadvantage attending the use of the reagent is the persistent foam which results after shaking and which must be allowed to subside before the volume of the gas is read. A few drops of alcohol at once dissipate the foam but spoil the reagent for further use. When alcohol is used the pipette must be carefully cleaned before another experiment.

In using this method the gas must first be freed from oxygen which is caused to unite with the hydrogen by the palladium, from unsaturated hydrocarbons which form addition products with the hydrogen, and from carbon monoxide which retards the absorption of the hydrogen. Bromine is recommended as the absorbent for the unsaturated hydrocarbons as it removes compounds of arsenic and phosphorus which might retard the catalytic action. Alkaline pyrogallate is advised for absorption of oxygen as phosphorus fumes affect the palladium. An ammoniacal solution of copper chloride is preferred to the acid solution.

8. General Scheme of Analysis.—Fig. 9 shows the apparatus ready for the analysis. The details concerning the individual steps of the process were given in Chapter II but it is well to recapitulate the important points in connection with the general

[1] *Zeit. Angewandt. Chem.*, 25, 1843 (1912).

scheme of analysis. The water of the burette is saturated with gas similar to that which is to be analyzed and a sample of approximately 100 c.c. is then drawn in and the volume read at atmospheric pressure after three minutes have been allowed to elapse so that the surplus water will have drained from the burette walls. Any needed correction for burette error is to be applied to this reading. The caustic soda pipette is to be con-

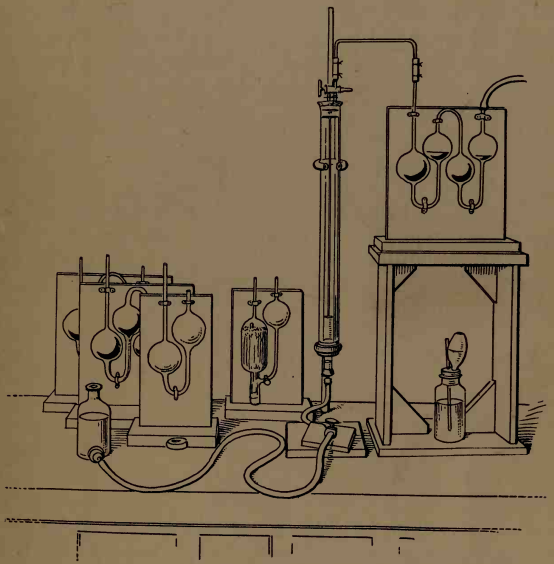

FIG. 9.—Assembled apparatus for gas analysis.

nected to the burette, and the gas passed into it and allowed to remain with gentle shaking for three minutes. CO_2 is absorbed, as well as H_2S, SO_2 etc., the whole being usually reported as CO_2. The gas is drawn back into the burette and while waiting for the excess water on the burette walls to run down, the capillary connecting tube is flushed out and the bromine water pipette

is connected. The volume in the gas burette is then read, and the gas passed into the bromine water where it is shaken for three minutes. It is drawn back to the burette, and at once passed into the caustic pipette where it is shaken one minute to remove bromine fumes. It is then drawn back into the burette and the decrease in volume reported as unsaturated hydrocarbons. The gas is next passed into the phosphorus pipette. White smoke at once appears. If it does not, it is a sign that some retarding catalyzer is present, usually removable by another treatment with bromine water. Following the estimation of oxygen comes that of carbon monoxide with cuprous chloride either acid or ammoniacal, preferably acid unless hydrogen is to be absorbed by palladium. Two cuprous chloride pipettes must be used in series, the second one containing almost fresh reagent. The residue from this absorption consists of hydrogen, hydrocarbons of the paraffine series and nitrogen. The hydrogen may be absorbed by palladium as outlined in this chapter but it is more common practice to estimate the hydrogen and hydrocarbons by combustion. The methods are discussed in the next chapter.

CHAPTER IV

EXPLOSION AND COMBUSTION METHODS FOR HYDROGEN, METHANE, ETHANE AND CARBON MONOXIDE

1. Available Methods.—Hydrogen and carbon monoxide may be estimated by absorption as indicated in the preceding chapter. They may also be estimated after oxidation to water or carbon dioxide. There are no satisfactory absorbents for methane and ethane and so these gases are always estimated indirectly after oxidation. The oxidizing agent may be gaseous oxygen and the reaction may be violent as in explosion methods or it may be quiet combustion. There may even be combustion of hydrogen

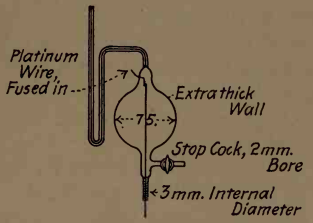

FIG. 10.—Detail of explosion pipette.

and carbon monoxide with the aid of a catalyzer in the presence of methane which remains unchanged. The oxidizing agent may also be an oxide, especially copper oxide, and here again there may be fractional combustion. The most rapid method and the one most frequently used is that of explosion.

2. Apparatus for Explosion Analysis.—The analysis by explosion is carried out in a stout glass vessel provided with electric connections across whose terminals a spark may be passed to cause the explosion. The shape and dimensions of the apparatus may vary. The form which has given good satisfaction

in the gas laboratory at the University of Michigan for a number of years[1] is shown in Fig. 10. It is a modification of the Hempel pipette and differs from it principally in the arrangement of the electric terminals and in the incorporation of an explosion guard in the stand.

In the older forms of pipette the explosion was induced by a spark made to jump a gap between two platinum wires sealed through the glass of the narrowed upper part of the bulb. When the interior of the bulb became wet as frequently happened the electric current would sometimes travel around the wet wall instead of sparking across the gap, and it was not possible to obtain an explosion. Gill[2] modified the bulb by introducing one of the wires through a ground glass joint at the bottom of the pipette. This was a valuable modification because it made the creeping distance so long that the spark was compelled to jump the gap, but the ground glass was difficult to keep tight. The form here described introduces the wire from the bottom but adopts a simple method of sealing which is very satisfactory. The lower wire which should be stiff (and may be of nickel about 1 mm. in diameter) is pushed through the open lower end of the pipette and sealed by sucking molten sealing wax into the pipette almost to the level of the tee. As the sealing wax hardens the wire may be moved to adjust the spark gap to the desired dimensions. No difficulty has been experienced in making this joint tight. The explosion pipette and its stand are shown in Fig. 11. The bulb is enclosed in a box open at the top and with a plate glass window in front, so that the operator can observe the explosion in perfect safety. The bottom of this box has an irregular opening sawed in it so that the pipette as shown in Fig. 10 may be lowered into place. The bulb sits in a cup shaped hollow of the shelf which may be padded with wet asbestos paper if necessary to make it fit well.

The weight of the mercury renders other fastening for the bulb unnecessary but the capillary is fastened to the rib behind it by a loop of fine copper wire passing through holes drilled in the rib. The strain of the rubber tube filled with mercury is taken off the glass tee by a ring below the shelf into which the rubber tube is

[1] White and Campbell, *J. Am. Chem. Soc.*, 27, 734 (1905).
[2] *J. Am. Chem. Soc.*, 17, 771 (1895).

wedged firmly by a split cork. The rack for the levelling bottle is higher than the tee of the pipette so that when the bottle is in the rack the mercury in the rubber tube is under pressure whereas if the mercury bottle were sitting on the base of the stand there would be a partial vacuum within the rubber tube. This may seem immaterial, but it must be remembered that all rubber is porous and that bubbles of air sucked into the rubber tube are certain to make their way up into the pipette and be measured

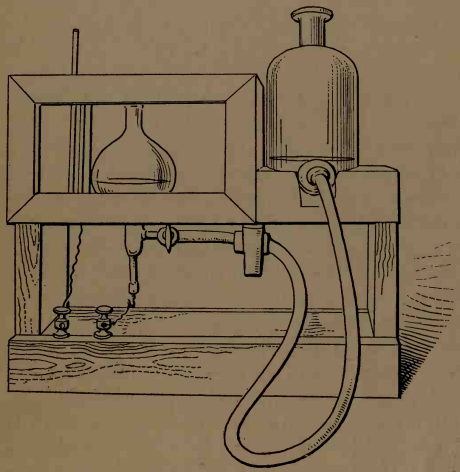

FIG. 11.—Explosion pipette and stand with protecting screen.

as part of the gas in it. Fine copper wires soldered to the electrode terminals of the pipette pass to the binding posts on the stand. The fine platinum electrode is liable to be cut if it is bent back and forth where it is sealed through the glass and to protect it the copper wire from the upper electrode is brought smoothly up to the capillary and tied there firmly with thread. The design of the stand is such that if a bulb breaks a new bulb may be inserted without trouble if it has even approximately the dimensions of the old one. The method of connecting this pipette to the burette and of transferring the gas is the same as for other

pipettes. This pipette is filled with mercury, since under the high pressure developed the solubility of the gases in water becomes large enough to cause appreciable error. An induction coil capable of giving a half inch spark together with its battery is necessary. A coil giving a large spark such as is given by the automobile sparkers is much better than a coil giving a thin high voltage spark.

3. Manipulation in Explosion Analysis.—In the explosion process a sample of gas previously freed from carbon dioxide, oxygen, unsaturated hydrocarbons and usually carbon monoxide is drawn into the burette and measured. Its volume may vary from 8.0 c.c. with pure methane to 50 c.c. with gases containing high percentages of nitrogen. Air sufficient to fill the burette is then drawn in. The burette is connected to the pipette as usual, care being taken to have the rubber connections in good condition and firmly wired, and the mixture is passed into the explosion pipette, the water of the burette being run over through the capillary of the pipette until the capillary is full. This water in the capillary acts as a cushion, preventing the force of the explosion from blowing up the rubber connections. The gas in the explosion pipette is brought to atmospheric pressure by means of the levelling bottle, the stopcock is closed, and the levelling bottle replaced in its rack. It is advisable to shake the pipette to ensure thorough mixing of the gases, for diffusion proceeds somewhat slowly. The gas is exploded by a spark from the induction coil. If the gas consists mainly of hydrogen there is usually no visible flame although a slight tremor of the mercury may be observed. If the gas contains much hydrocarbon a flash of flame may usually be seen. It is not advisable to spark the mixture more than a second as some nitrogen will unite with the oxygen at the temperature of the spark forming oxides of nitrogen with decrease of volume and erroneous results. The explosion completed, the gas is again brought to atmospheric pressure by means of the levelling bottle, and then brought back into the burette and measured. If there has been marked contraction, the next step is to pass the gass into caustic solution and determine if there has been formation of carbon dioxide.

If the decrease in volume after explosion was less than 12 c.c. it is almost certain that the explosion was incomplete. If

there was no decrease in volume it is not safe to assume that no combustible gas was present, for it may have been present in such a small proportion that the mixture was not explosive. The proper procedure in either case is to add about 10 c.c. of pure hydrogen made by the action of caustic potash on metallic aluminum and explode a second time. The addition of this amount of hydrogen ensures complete explosion. After allowance for the contraction due to the added hydrogen, the composition of the original gas may be calculated as explained later.

It is advisable to determine roughly the amount of oxygen remaining after the explosion so that there may be no doubt that an excess was present.

4. Oxidation of Nitrogen as a Source of Error.—Almost all technical gases contain nitrogen as do also commercial forms of oxygen. Bunsen first noted that nitrogen and oxygen react at the temperature of the electric spark or of an explosion flame to form small amounts of various oxides of nitrogen whose volume is less than that of the reacting gases and which combine with caustic. The formation of oxides of nitrogen leads, therefore, to an erroneously high contraction after explosion and to an erroneously high figure for CO_2 due to explosion. The error is discussed more fully in Chapter VI on Exact Gas Analysis but it cannot be altogether neglected in technical work. The error increases with higher flame temperatures and the simplest way to keep it within reasonable limits is to dilute the reacting gases with some inert gas such as nitrogen or excess of oxygen. The volume of the gases participating in the explosion (combustible gas + theoretical volume oxygen) should be from one-third to one-fifth that of the non-exploding gases (nitrogen + excess oxygen). It will be seen that 12 c.c. H_2 + 6 c.c. O_2 require to be diluted with from 54 to 90 c.c. nitrogen or oxygen and that 8 c.c. CH_4 + 16 c.c. O_2 require at least 72 c. c. of diluting gases.

The explosion of large samples of gas mixed with commercial oxygen, a method proposed by Hinman and endorsed by Gill,[1] involves much greater danger of blowing up the pipette and because of the higher temperature of explosion, tends to cause a larger formation of oxides of nitrogen from the nitrogen necessarily present.

[1] *J. Am. Chem. Soc.*, 17, 987 (1895).

5. Accuracy of Explosion Methods.—The necessity of diluting the exploding gases to avoid oxidation of nitrogen restricts the size of a sample of a rich gas like illuminating gas to about 10 c.c. With this small sample each 0.1 c.c. error in reading means 1.0 per cent. A greater accuracy can therefore not be expected except by averaging a number of analyses. It may be considered safe to rely upon a single analysis for the various gases determined by absorption, but explosion analyses should always be made in duplicate. The main portion of the gas after the absorption should be stored in a gas holder to be drawn upon for subsequent check analyses.

6. Hydrogen by Explosion.—If hydrogen is the only combustible gas taking part in the explosion its volume may be calculated from the contraction after explosion according to the following equation:

$$2H_2+O_2=2H_2O$$
$$2+1 \ =2 \text{ or } 0$$

Expressed in volumes this means that two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapor. Since, however, the gas after explosion cools again to the temperature of the burette water and is the same as before explosion, and since it was saturated with water before explosion, the additional water formed must all condense. For our purposes, therefore, two volumes of H_2 react with one volume of O_2 with complete disappearance of the reacting gases. Under these circumstances when hydrogen is the only exploding gas, two-thirds of the resulting contraction will be the volume of the hydrogen exploded.

7. Hydrogen and Methane by Explosion.—Methane combines with two volumes of oxygen to form carbon dioxide and water according to the following equation:

$$CH_4+2O_2=CO_2+2H_2O$$
$$1+2 \ = 1 \ + \ 0$$

The volumetric relations are expressed by the figures of the equation, one volume of methane uniting with two of oxygen to form one volume of carbon dioxide, and two of water vapor

which condense and disappear as explained in the preceding paragraph. The result of the explosion, therefore, is that there is a contraction of two volumes for every one volume of methane and the formation of a volume of carbon dioxide equal to the methane.

It is possible to determine the proportion of hydrogen and methane present in a gas mixture by explosion with air. The volume of carbon dioxide resulting from the explosion equals the volume of the methane. The contraction due to the methane is twice the volume of the methane and the difference between this contraction in volume and the total contraction is the contraction due to the explosion of hydrogen. In accordance with the preceding section two-thirds of this contraction is hydrogen. The following example will serve as an illustration of the method of calculation.

Sample of illuminating gas	99.5	c.c.
Volume after absorption of CO_2, C_nH_{2n}, O_2, CO		85.2
Sample for explosion	10.3	
Air to		97.6
After explosion, volume	80.1	
Contraction		17.5
After KOH, volume	74.9	
Vol. CO_2 formed		5.2
After phosphorus, volume	69.4	
Vol. excess oxygen		5.5

Calculation 5.2 c.c. $CO_2 = 5.2$ c. c. CH_4

Contraction due to 5.2 c.c. $CH_4 = 2 \times 5.2 = 10.4$

Contraction due to hydrogen $= 17.5 - 10.4 = 7.1$

Hydrogen $= 2/3 \times 7.1 = 4.7$

Vol. $CH_4 = 5.2$

Vol. $H_2 = 4.7$

Vol. N_2 by diff. 0.4

10.3

$$\text{Per cent. } CH_4 = 5.2 \times \frac{85.2 \times 100}{10.3 \times 99.5} = 43.1$$

$$\text{Per cent. } H_2 = 4.7 \times \frac{85.2 \times 100}{10.3 \times 99.5} = 39.0$$

$$\text{Per cent. } N_2 = 0.4 \times \frac{85.2 \times 100}{10.3 \times 99.5} = 3.3$$

The ratio of exploding to non-exploding gases in the above illustration may be calculated as follows:

Exploding gases 5.2 c.c.	$CH_4+10.4$ c.c.	$O_2=15.6$
4.7 c.c.	$H_2+2.35$ c.c.	$O_2=7.05$

Exploding gases	22.65
Non-exploding gases $97.6-22.65=74.95$	
exploding gases / non-exploding gases	$\frac{22.65}{74.95}=\frac{1}{3.3}$

The excess of oxygen is calculated from the volume of air taken for explosion, $=97.6-10.3=87.3$ c.c. air with 20.9 per cent. $O_2=$ 18.24 c.c. O_2 available. Used for combustion, as above, $10.4+2.35=12.75$ c.c. Excess oxygen $=$ $18.24-12.75=5.49$ c.c., which checks with the 5.5 c.c. found by direct experiment.

8. Carbon Monoxide, Hydrogen and Methane by Explosion.— The composition of a gas mixture containing CO, H_2, and CH_4 may be determined by a single explosion if in addition to the contraction and CO_2 the oxygen used in the explosion is also determined.

There are various methods of calculation, that given by Noyes and Shepherd[1] being as follows:

1. Gas taken	$=CH_4+CO+H_2+N_2$
2. Contraction	$=2CH_4+\frac{1}{2}CO+\frac{3}{2}H_2$
3. Oxygen consumed	$=2CH_4+\frac{1}{2}CO+\frac{1}{2}H_2$
4. CO_2 formed	$=CH_4+CO$

Hence $H_2=$ Contraction $-O_2$ consumed.

$CO=\frac{2}{3}$ ($2CO_2+\frac{1}{2}H_2-O_2$ consumed)

$CH_4=CO_2-CO$

$N_2=$ Total gas $-(H_2+CO+CH_4)$.

The oxygen consumed is calculated by determining the residual oxygen and deducting this from the volume of oxygen introduced as air whose percentage of oxygen is assumed to be 20.9.

This method is more rapid than the usual one in which the CO is absorbed by Cu_2Cl_2, and it has no systematic errors, provided the dilution is great enough to avoid oxidation of nitrogen. It will, except in expert hands, be found less reliable

[1] *J. Am. Chem. Soc.* 20, 345 (1898).

than the usual method of absorption of CO and explosion of H_2 and CH_4 because each value calculated is dependent on the accuracy of three successive operations instead of two.

9. Quiet Combustion of a Mixture of Oxygen and Combustible Gas.—Various attempts have been made to do away with the explosion pipette by causing the gas to burn gradually. Coquillion[1] in 1876 proposed to estimate small amounts of hydrocarbons in the air from mines by placing within a pipette a spiral of platinum or palladium wire. The mine air was introduced into the pipette, the spiral was to be heated to redness and, the amount of combustible gas being below the explosive ratio, the hydrocarbons were to be gradually burned. He recommended that for technical gases where there was danger of explosion the platinum spiral be placed in a small bulb blown

FIG. 12.—Quartz combustion tube with platinum spiral.

in the capillary tube between the burette and pipette. The mixture of gas and air was measured in the burette, and then passed through the capillary over the glowing spiral. The capillary tube was supposed to be adequate to prevent the explosion from flashing back into the burette. Hempel[2] has improved this latter apparatus by placing the platinum spiral in a quartz tube between two glass capillary tubes. His arrangement as modified by the author is shown in Fig. 12 where *AB* represents a tube of transparent quartz about 4 mm. internal diameter and 125 mm. long, at each end of which are glass capillary tees connected to it by rubber tubing. Through each tee runs a stout nickel wire connected by a spiral of fine platinum wire. The nickel wires are sealed into the glass capillaries by sealing wax drawn into the enlarged ends of the capillaries. The apparatus may therefore be readily repaired if the platinum

[1] *Comptes rendus*, 83, 394; 84, 458 and 1503.
[2] *Zeit. angewandt. Chem.*, 25, 1841 (1912).

wire becomes burned out. The nickel wires should be so large that they almost fill the capillary tube which should be of about 1 mm. internal diameter. They will then not be heated perceptibly by the passage of an electric current sufficient to heat the platinum wire to redness and will by their cooling action help to prevent the explosion from flashing back into the gas burette. If the mixture of gas and air is passed slowly over the platinum spiral the temperature will not rise above a fair red heat and there will be little danger of formation of oxides of nitrogen, hence there is no need of diluting the gases with so much air as is necessary in the explosion process and therefore a larger sample of gas may be used. It is not safe, however, to take a large sample of gas and dilute it with pure oxygen, for the capillary tube cannot be relied upon to prevent an explosion flashing back into the burette when a very explosive mixture is used.

The inaccuracy of the usual explosion methods led Dennis and Hopkins[1] to devise a process of combustion whereby a large sample of gas might be quietly burned in pure oxygen. The combustion pipette consists of a pipette such as is used for phosphorus with its second bulb cut off and a levelling bottle for mercury connected. The ignition wire in the form of a platinum coil or grid is placed within the pipette immediately under the gas inlet and connected to two heavy wires which, insulated from each other, pass through the rubber stopper at the bottom of the pipette and are fastened to binding posts. The diameter and length of the platinum ignition wire must be chosen with reference to the electric circuit so that it will be easily heated to redness and its temperature controlled without the need of cumbrous rheostats. The conducting wires within the pipette may be of platinum or one of the non-rusting nickel-chromium alloys and should be at least 1 mm. in diameter.

The manipulation is as follows. The full volume of gas remaining after absorption of oxygen, consisting of CO, H_2, CH_4 and N_2 is transferred to the combustion pipette and a clamp is screwed onto the rubber connecting tube at the tip of the burette so that the pipette may be disconnected from the burette. The burette is filled with oxygen free from CO_2 and

[1] *J. Am. Chem. Soc.*, 21, 398 (1899).

of known purity and reconnected to the pipette, but the stopcock of the burette is kept closed. The levelling bottle of the pipette is placed at such a height that the gas in the pipette is under slightly diminished pressure and the electric ignition wire brought to incandescence. The stopcock on the burette is now opened and a slow stream of oxygen passed into the pipette. A slight flash is usually noticeable as ignition takes place and the platinum wire glows more brightly so that it may be necessary to interpose more resistance in the heating circuit. The volume of gas in the pipette may either increase or decrease and the height of the levelling bottle must be varied accordingly. It is usually necessary to periodically increase the external resistance to prevent the platinum wire from burning out as the hydrogen originally present gives way to water vapor. After the oxygen is all passed into the pipette, the current is interrupted, the gases allowed to cool and the CO, H_2 and CH_4 determined as in § 8.

The great advantage of this process lies in the large sample and the consequent diminution of the error of observation. It requires a special pipette, which is, however, easily constructed, a source of electric current and a controlling rheostat. The manipulation is somewhat complicated and it has been the author's experience that novices usually wish that nature had provided them with an extra pair of hands. The error due to oxidation of nitrogen has been found by the author[1] to be fully as large in this process as in the explosion process. The subject is discussed more fully in Chapter VI. Hempel[2] also reports unfavorably on this process on account of the formation of oxides of nitrogen when combustion is continued long enough to ensure oxidation of all the methane.

10. Fractional Combustion with Palladinised Asbestos.—The well known power of palladium to bring about the union of hydrogen and oxygen at low temperature has long been made use of as a means of separating hydrogen from methane. The use of palladinised asbestos is due to Winkler. The asbestos is prepared by soaking a small amount of selected long fibered asbestos in a concentrated solution of palladous chloride prepared according to § 7 of Chapter III. The fibers are to be kept as

[1] *J. Am. Chem. Soc*, 23, 477 (1901).
[2] *Zeit. Angewandt. Chem.*, 25, 1841 (1912).

nearly parallel as possible and after saturation are to be dried and ignited at a very dull red heat when the chloride will decompose leaving the fibers coated with metallic palladium and possibly palladous oxide. A bundle of two or three of these single fibers about an inch long is introduced into the end of a straight capillary glass tube about 1 mm. internal diameter and eight inches long, and brought to the middle of the capillary by suction on the opposite end of the tube. A drop of water on the asbestos makes it move more freely. The capillary is then to be dried and bent to the usual form for connecting the burette and pipette.

In manipulation 20 or 30 c.c. of gas freed from CO_2, C_nH_{2n} and usually CO is mixed with an excess of air and passed through the capillary tube containing the palladinised asbestos into a pipette containing water. If the asbestos is very active, combustion may begin without external heat but to make certain the tube is heated with a small gas flame or alcohol lamp. It is not necessary to heat the tube to redness. A spark frequently appears at the end of the asbestos filament when the combustible gas first strikes it. This is a sign that the gas is passing too rapidly and the speed must be decreased until the spark disappears. Otherwise some methane will be burned. The gas is passed back and forth through the capillary twice and then drawn back into the burette and the volume measured. If hydrogen alone has been burned two-thirds of the contraction will be the volume of the hydrogen as explained in § 6. Carbon monoxide will burn as well as hydrogen in this process and where both were present, it will be necessary to determine the carbon dioxide formed in addition to the contraction. The calculations follow from the equations:

$$2CO + O_2 = 2CO_2$$
$$2 + 1 = 2 \qquad \text{Contraction} = \tfrac{1}{2}CO \text{ or } \tfrac{1}{2}CO_2$$
$$2H_2 + O_2 = 2H_2O$$
$$2 + 1 = 0 \qquad \text{Contraction} = \tfrac{3}{2}H_2$$

Therefore $CO_2 = CO$

$$\text{Total contraction} = \tfrac{1}{2}CO + \tfrac{3}{2}H_2$$
$$H_2 = \tfrac{2}{3}\ (\text{contraction} - \tfrac{1}{2}CO)$$

This method is accurate provided the palladinised asbestos is dry and active and the proper temperature is maintained. It requires care to prevent any drops of water from getting into the capillary. If this happens when the capillary is cold the thread of asbestos becomes wet and must be dried thoroughly before it is active. If a drop of water gets into the capillary while it is hot the glass tube cracks. Very little attention has been paid to the possibility of small amounts of foreign gases rendering the palladium catalyzer inactive, but from the elaborate precautions which are necessary to keep the platinum contact substance active in the sulphuric acid manufacture it is evident that this possibility should not be ignored. The capillary tube should never be heated to redness on account of danger of burning methane. The combustible gases are diluted largely with air to avoid too intense combustion and also to avoid an explosion of the main body of the gas which might be propagated through the capillary if the gas mixture were too rich. Disastrous explosions have been known to result from an attempt to burn mixtures of hydrogen and oxygen in this manner. The combined volumes of hydrogen and carbon monoxide in the sample taken for analysis should not be over 20 c.c. and the volume after dilution with air should be almost 100 c.c. This method has been investigated by Nesmjelow[1] who emphasizes the danger of burning methane if the gases are passed through the capillary at a rate faster than one liter per hour. Hempel[2] has recently reported the results of a study of this process and finds that to obtain accurate results the temperature of the capillary must not rise over 400° C. and that the gas must be passed at a speed of not over 100 c.c. in eight minutes. He recommends, as a method of temperature control, that the portion of the capillary to be heated rest in a brass trough which in the middle is thickened sufficiently to contain a hole deep enough for a thermometer bulb. In default of a thermometer a glass tube sealed at the bottom and containing a little mercury may be inserted in the hole. The boiling of the mercury (358° C.) indicates when a sufficiently high temperature has been reached.

[1] *Zeit. Anal. Chem.*, 48, 232 (1909).
[2] *Zeit. Angewandt. Chem.*, 25, 1841 (1912).

11. Fractional Combustion with Copper Oxide.—The combustion of carbon compounds of all sorts through contact with hot copper oxide has been a method long employed by organic chemists. Campbell[1] first utilized the principle of fractional combustion in gas analysis and determined accurately the minimum combustion temperature for various gases both with copper oxide alone and with palladinised copper oxide. His values are as follows:

Gas	Initial combustion point	
	Pure CuO	Pd.-CuO
H_2	175–180° C.	80–85° C.
CO	100–105° C.	100–105° C.
C_2H_4	315–325° C.	240–250° C.
C_3H_6	270–280° C.	220–230° C.
C_4H_8 (Iso)	320–330° C.	270–280° C.
CH_4	Nc combustion at 455° C.	

Jaeger[2] first proposed a convenient scheme for utilizing this principle in ordinary gas analysis and the method usually bears his name. He takes advantage of the wide difference in the ignition point of CO and H_2 as compared with CH_4 to separate the two gases by fractional combustion. His method with some modifications which the author has found desirable is as follows:

The combustion tube shown at A in Fig. 13 is of hard Jena glass or preferably transparent quartz and has an internal diameter of about 10 mm. and a length of 200 mm. It is filled throughout its middle 100 mm. with granulated copper oxide kept in place by wads of asbestos fiber. The open ends of the tube are closed by elbows of glass capillary tubing which slip within each end of the combustion tube as far as the asbestos wads and are held in place by rubber tubing fitting tightly over the end of the combustion tube and also over the glass capillary. The asbestos shield shown in section at B and in elevation at C sits like a saddle over the middle portion of the tube and keeps the heat from the rubber connections during combustion. The combustion gases pass out the perforations shown in the top of the shield. A thermometer standing in the tube of the

[1] *Am. Chem. Jour.*, 17, 688 (1895).
[2] *Jour. Gasbeleucht*, 41,764 (1898).

shield with its bulb touching the combustion tube indicates the temperature at which hydrogen is being burned.

The whole volume of the gas from which CO_2, C_nH_{2n} and O_2 have been removed is used for the analysis. The copper oxide tube is connected to the burette on one side and on the other to a phosphorus pipette which has been previously filled with air and now contains nitrogen. This nitrogen is allowed to flow through the combustion tube and out into the air through the burette stopcock flushing out the air in the tube and rendering

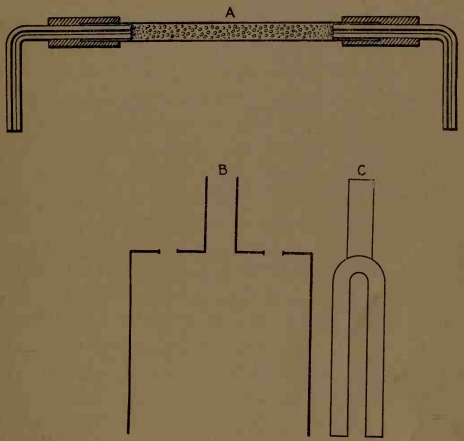

FIG. 13.—Quartz combustion tube filled with copper oxide.

unnecessary the troublesome correction involved in Jaeger's original method. The nitrogen is all driven out of the phosphorus pipette, and the water in it blown to a mark arbitrarily fixed on the capillary stem of the pipette and the burette stopcock turned so that connection with the outside air is shut off, the burette also remaining closed. The gas burner under the combustion tube is lighted and adjusted so that the thermometer inserted in the jacket and resting on the combustion tube shows about 250° C. The expanding nitrogen in the combustion tube is free to pass into the phosphorus pipette. When the

combustion tube is hot, the burette stopcock is opened and the gas passed slowly into the phosphorus pipette and back again so that it has all been exposed twice to the action of the copper oxide. A few cubic centimeters of the gas are again passed into the phosphorus pipette, the burette stopcock is closed and the flame removed. If the combustion tube is of glass it must be slowly cooled to room temperature but if it is of quartz it may be sprayed with water or wrapped with a wet cloth until it again reaches room temperature. As the tube cools there is sucked back from the pipette some of the gas purposely placed there and when it is thought that the tube has reached room temperature the liquid of the pipette is again brought to the mark in the capillary which was used at the commencement of the test. If after adjustment has been made the water of the pipette continues to rise in the capillary it is proof that the combustion tube has not yet reached room temperature.

The volume of the gas in the burette is now measured and a caustic potash pipette substituted for the phosphorus pipette. This requires somewhat careful manipulation for the combustion tube is still filled with gas which must not be allowed to diffuse into the air. To accomplish the substitution the stopcock of the burette is opened and the gas drawn out of the capillary of the phosphorus pipette into the burette until the liquid has mounted as high as the rubber connecting tube. The glass capillaries of the pipette and the combustion tube are separated enough to allow a clamp to be screwed on the rubber tube and the phosphorus pipette is disconnected and replaced by a caustic pipette whose liquid before making the connection is blown practically to the top of the capillary by the help of a rubber tube attached to the second bulb. With care this substitution of one pipette for the other may be made with an error of only a few tenths of a cubic centimeter. The carbon dioxide formed from the CO is then determined. Since it is not feasible to drive all the gas from the combustion tube into the caustic the gas should be passed back and forth several times. The method of calculation of the H_2 and CO follows from the equations:

$$H_2 + CuO = H_2O + Cu$$
$$CO + CuO = CO_2 + Cu$$

The metallic copper has practically the same volume as the copper oxide. The CO_2 has the same volume as the CO. The H_2 completely disappears. Therefore the contraction in volume after heating to 250° is equal to the H_2, and the CO_2 is equal to the CO.

Methane is estimated by heating the combustion tube to redness and slowly passing the gas back and forth into the caustic pipette. Methane burns somewhat slowly and it is wise to pass it back and forth at least four times. The decrease in volume is read after the combustion tube has been cooled as before. The equation for the reaction is:

$$CH_4+4CuO=4Cu+CO_2+2H_2O.$$

If the gas had been passed back and forth into a pipette filled with water during the combustion there would have been no change in volume but since the gas was passed into the caustic pipette during the combustion process and the CO_2 was absorbed the contraction equals the methane.

It is assumed in this calculation that CH_4 is the only one of the paraffine series present. This is usually the case but natural gas, Pintsch gas, carburetted water gas and gas from coal distilled below a red heat may contain small proportions of ethane and possibly higher homologues. Pentane vapors are present in many samples of natural gas. Any two constituents such as methane and ethane may be determined by this method if during the combustion at a red heat the gases are passed back and forth into the phosphorus pipette or other pipette filled simply with water and the contraction after combustion measured and then the CO_2 determined. The calculation follows from the equations:

$$CH_4+4CuO=4Cu+CO_2+2H_2O.$$
$$C_2H_6+7CuO=7Cu+2CO_2+3H_2O.$$

In the case of CH_4, the volume is the same after combustion as before. In the case of C_2H_6 the volume has increased by a volume of CO_2 equal to the C_2H_6. Any increase in volume after combustion is reported as C_2H_6 and the volume of the CO_2 less twice the C_2H_6 is reported as CH_4.

In case pentane is present the increase of volume after com-

bustion is four volumes for each volume of pentane according to the equation—

$$C_5H_{12}+16CuO=5CO_2+6H_2O.$$

It is not usually feasible to distinguish by analysis between the various higher hydrocarbons.

The copper oxide has been partially reduced to metallic copper in the combustion and must be re-oxidized by drawing air through the red hot tube. This may be done very conveniently by means of an aspirator since no attention on the part of the analyst is required.

This method is perhaps the most accurate of the technical methods for the estimation of CO, H_2 and CH_4 and is to be commended because it does not involve any special equipment which cannot be made by the analyst himself. It is somewhat slower than the explosion methods but if a quartz tube is available it is not a tedious process. A quartz tube is highly desirable since glass tubes always break after a time and in breaking usually spoil the analysis. There is no danger of oxidation of nitrogen as in the other methods and a large sample of gas may be taken thus reducing the errors of observation to a minimum. The greatest liability to error comes from incomplete combustion of the hydrocarbons. Ethane is especially difficult to burn and it is desirable to repeat the combustion on the gas residue after the CO_2 has been absorbed to make sure that there is no further formation of CO_2.

12. Nitrogen.—There is no desirable method for the direct determination of nitrogen, which is always taken by difference. This is very unsatisfactory since, although some of the errors in analysis may compensate each other, there is a tendency in a long analysis for them to pile up on the nitrogen.

The Jaeger method of combustion with copper oxide just described allows all of the gases other than nitrogen to be removed in a single process and affords a valuable check on the accuracy of the longer anaylsis. A sample of 100 c.c. of the gas to be analyzed is passed through the combustion tube at red heat and into caustic. The CO_2, CO, H_2, and C_nH_m will all disappear in the process as will also the oxygen if it is present in

only small amount. The residue will be nitrogen and possibly oxygen which may be removed by phosphorus.

13. Form of Record of Gas Analysis.—There may of course be great variation in methods of keeping records of gas analyses. The record should in every case however be full enough to show every step of the operation. The following record is given as a sample.

ANALYSIS OF ILLUMINATING GAS

at Chemical Laboratory, University of Michigan, Sept. 9, 1907

Sample	99.4−0.3=99.1 c.c.		
After KOH	97.4	CO_2 =2.0 c.c.	=2.0%
After Br_2	92.6	C_2H_4, etc., 4.8 c.c.	4.8
After P	92.2	O_2 0.4 c.c.	0.4
After Cu_2Cl_2	84.8−0.3=84.5	CO 7.4 c.c.	7.5

First explosion:			
Sample	9.4−0.3= 9.1		
Air to	97.9−0.3=97.6		
After explosion	83.0	Contraction	=14.9
After KOH	79.2	CO_2	= 3.8
After P	71.0	Excess O_2	= 8.2

Calculations:

Factor to give percentage $\frac{84.5\times100}{9.1\times99.1}=9.37$

$CH_4=3.8\times9.37$ =35.6%

$H_2=2/3(14.9-2\times3.8)9.37$ =45.6%

$N_2=[9.1-(3.8+4.87)]9.37$ = 4.0%

Exploding gases:

3.8 c.c. CH_4+7.6 c.c. O_2 =11.4 c.c.

4.9 c.c. H_2 +2.4 c.c. O_2 = 7.3 c.c.

18.7

Non-exploding gases:

97.6−18.7 78.9

Ratio $\frac{\text{non-exploding}}{\text{exploding}}=\frac{78.9}{18.7}=4.2$

Second explosion:			
Sample	9.2−0.3= 8.9 c.c.		
Air to	95.0−0.3=94.7		
After explosion	80.4	Contraction	14.6
After KOH	76.7	CO_2	3.7
After P	70.0	Excess O_2	6.7

Calculations:

Factor to give percentage $\frac{84.5\times100}{8.9\times99.1}=9.58$

$CH_4 = 3.7\times9.58 = 35.4\%$
$H_2 = 2/3(14.6-2\times3.7)9.58 = 46.0$
$N_2 = [8.9-(3.7+4.8)]9.58 = 3.8$

Exploding gases:

3.7 c.c. CH_4 + 7.4 c.c. O_2 = 11.1 c.c.
4.8 c.c. H_2 + 2.4 c.c. O_2 = 7.2

18.3

Non-exploding gases:

$94.7-18.3 = 76.4$

Ratio $\frac{\text{non-exploding}}{\text{exploding}} = \frac{76.4}{18.3} = 4.2$

Summary of analysis:

	I	II	Average
CO_2	2.0		2.0%
C_2H_4, etc.,	4.8		4.8
O_2	0.4		0.4
CO	7.5		7.5
CH_4	35.6	35.4	35.5
H_2	45.6	46.0	45.8
N_2	4.0	3.8	3.9
			99.9%

CHAPTER V

VARIOUS TYPES OF APPARATUS FOR TECHNICAL GAS ANALYSIS

1. Introduction.—Chapter II describes the apparatus which the author believes best adapted to technical gas analysis and gives detailed directions for its manipulation. The present chapter will describe various other forms of technical apparatus especially those which first embodied valuable principles. The number of modifications is legion and no attempt will be made to even enumerate them. The order of description will in general be historical.

2. Schlösing and Rolland's Apparatus.—Perhaps the earliest

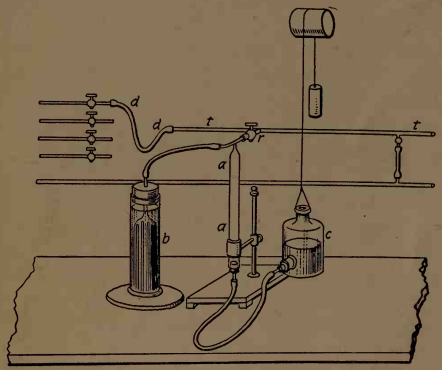

FIG. 14.—Schlösing and Rolland's apparatus.

successful attempt to devise an apparatus for the rapid analysis of industrial gas was that of Schlösing and Rolland[1] who devised a simple apparatus which foreshadowed closely the modern type. Their apparatus apparently attracted little attention

[1] *Annales de. Chim.*, Series 4, t.14, 55 (1868).

partly because its description was embodied in a long article on the ammonia-soda process whose title did not contain any reference to gas analysis. The original cut of their apparatus is reproduced as Fig. 14 as it still may serve as a model for a chemist who has to improvise his own apparatus. The following description of the apparatus is taken from the original work. In the upper left hand corner of the cut are seen four lead pipes of small diameter coming from various pieces of apparatus in the plant. A rubber tube *d* connects any one of these with the copper tube *t* to which is attached an aspirator. The burette *a* terminates at the top in a tee of almost capillary tubing, one arm of which connects to the gas supply through the cock *r* and the other to the pipette *b*. No mention is made of a clamp on the rubber tube between *a* and *b* but necessarily such must have been used. To draw a sample of gas the cock *r* is opened and the levelling bottle *c* is raised until the water fills the burette and reaches *r*. The gas formerly in the burette is now in the pipe *t* out of which it is swept by the stream of gas which is constantly flowing. The bottle is then lowered until the gas has passed below the 100 mark. The aspirator is stopped, the rubber tube *d* disconnected and the bottle raised, *r* being again opened until the level of the water in the burette is at 100 and is at the same time coincident with the level of the water in the levelling bottle. The burette will then contain 100 volumes of gas at atmospheric pressure. The gas is then passed back and forth into the absorption pipette *b* filled with caustic potash and containing glass tubes to increase the absorptive surface. The volume in the burette is then read as before and the decrease in volume reported as CO_2.

3. Orsat's Apparatus.—The original form of the Orsat[1] apparatus is practically the same as that frequently used today, as will be seen by Fig. 15 which is a reproduction of the original cut. It consists of a water-jacketed gas burette terminated at its upper end by a branched glass capillary tube. The pipettes, in order from right to left, contain caustic potash, alkaline pyrogallate and cuprous chloride. The cock I on the branched capillary serves for the connection of a platinum capillary in which hydrocarbons mixed with air, and added hydrogen if necessary, may be burned. The sample of gas is brought to the burette by the water-aspira-

[1] *Annales des Mines*, Series 7, t.8, 485 (1875).

tor KLM which sucks a rapid stream of gas through the cock R and the dust filter P. The operation of the apparatus will be evident to anyone who has read the three preceding chapters.

Many modifications of this burette have been prepared since it was first described, but the principle has not been altered. One group of workers has increased the complexity of the apparatus in an attempt to increase speed of manipulation. The most noteworthy change of this sort is probably the introduction of the

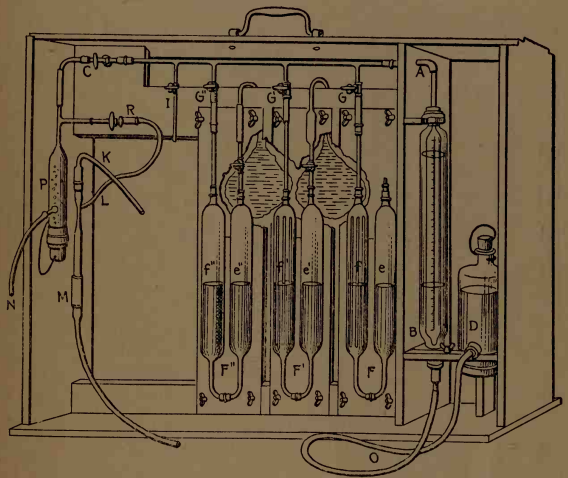

FIG. 15.—Orsat apparatus. Original form.

bubbling pipette in which, by a three-way cock on the top of each pipette, the gas is made to pass down a central tube and bubble up through the liquid of the pipette to be later drawn from the top of the pipette when the three-way cock is thrown to its second position. There are decided objections to complication in any form of apparatus which may receive rough treatment in transportation and which is frequently handled carelessly by its operators.

The usual modifications of the Orsat apparatus possess at least four glass stopcocks on the various outlets of the branched tee.

Unless the apparatus is always manipulated by a skilled operator it is almost inevitable that some of the alkaline reagent from the pipettes will be drawn into these stopcocks. It is apparently equally inevitable that the cocks will as a consequence stick and become broken. The branched tee is itself a source of trouble since it is fragile and difficult to clean when stopped. In Fig. 16 is shown a modification of the Orsat apparatus due to Allen and Moyer which commends itself for its simplicity and durability. The capillary glass tube is replaced by one of hard rubber and the glass stopcocks are replaced by pinchcocks which are practically as satisfactory. The pipettes themselves are of the test tube type and are closed at the top with a soft rubber stopper which is pressed against the upper shelf by the screw which supports the cup in which each pipette rests. This gives a firm and yet elastic support for the pipettes which prevents breakage in shipment.

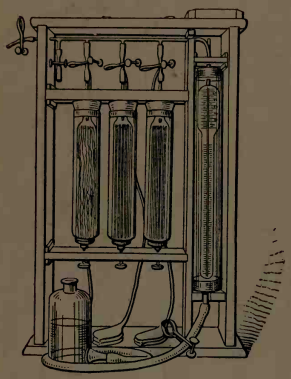

FIG. 16.—Orsat apparatus. Allen-Moyer modification.

The method of operating all Orsat burettes is the same. The water of the burette should be saturated with gas similar to that which is to be analyzed. The gas is taken into the burette through the end of the capillary projecting out of the left hand side of the case. If the sample is drawn directly from the smoke flue the precautions given in Chapter I on Sampling must be observed. In any case the burette is filled with gas which is then wasted through the fourth side arm into the outside air, thus getting rid of the air which was in the capillary tube of the instrument. The sample of gas is now drawn into the burette and measured with the precautions given in Chapter I. In addition to the gas which is in the burette there is a volume of about 1 c.c. in the capillary tube which is entirely neglected. The gas is passed into the caustic pipette and CO_2 determined

as described in § 1 of Chapter III, then into the second pipette filled with pyrogallate for oxygen (§ 4 of Chapter III), then into the third pipette filled with cuprous chloride for CO (§ 6 of Chapter III).

This apparatus is much used for analysis of smoke gases and it is sufficiently accurate for this purpose. The errors which arise from the failure of the gas in the capillary to come into contact with the reagent will hardly be more than 0.1 c.c. for each of the gases. The tendency will be for the oxygen to be slightly high due to some CO_2 which did not get into the caustic pipette and for the CO to be high due to oxygen which did not get into the pyrogallate pipette.

The Orsat apparatus is not usually employed for gases like illuminating gas where many constituents have to be determined, although other absorption pipettes and even explosion pipettes have sometimes been made a part of the instrument. The errors mentioned above due to the gas remaining in the capillary increase with the length of the capillary and it becomes preferable to use the burette with detachable pipettes.

4. Bunte's Burette.—Dr. H. Bunte[1] in 1877 described his burette which although in the main obsolete still has some uses and is illustrated in Fig. 17. It consists of a burette closed at the top by a three way cock *a* carrying a funnel tube, and at the bottom by a cock *b*. The zero of the burette is somewhat above the lower cock.

A levelling bottle such as is used with the ordinary Hempel type of gas burette is to be connected to the lower cock. The sample of gas is drawn into the burette as usual and its volume may be read as usual. The method of reading the volume prescribed by Bunte is unusual. A sample of gas slightly larger than 100 c.c. is to be taken into the burette and the volume compressed until it reads exactly 100. Water is now poured into the funnel tube to the mark *m* etched upon it and cock *a* is opened to communicate with the funnel tube which is unstoppered. Some gas bubbles through the cock and the liquid above it and escapes into the air. The bore of the cock is so small that no water flows down and after the bubbling has ceased the volume of gas in the burette is still 100 c.c. measured under the pressure

[1] *Jour. für Gasbel.*, 1877, 447.

of the atmosphere plus the column of water in the funnel tube. The volume of the gas is always to be read under these conditions. In order to introduce an absorbent such as NaOH into the burette a partial vacuum is produced by opening the lower cock and lowering the levelling bottle. The cock *b* is then closed, the levelling bottle disconnected and the reagent in a small dish is placed below the cock *b* so that the tip of the cock is immersed. On opening the cock some of the reagent will be sucked into the burette. The burette is then shaken to facilitate absorption, care being taken to hold it only by the tips so that the heat of the hands will not change the temperature of the gas. To read the volume after absorption the funnel tube on the top of the burette is again filled with water, and the upper cock opened. Water flows into the burette and more water is added to the funnel until with the upper cock still open the water remains stationary on the mark *m*. Conditions are now as they were at the first reading and the volume is again read. The diminution in volume if NaOH was the reagent, is as usual reported as CO_2.

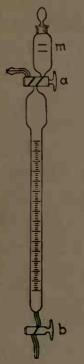

FIG. 17.—Bunte gas burette.

Oxygen is determined by alkaline pyrogallate (§ 4 of Chapter III). To avoid diluting the reagent the dilute caustic in the burette is sucked out as far as possible and 20 c.c. of the pyrogallate introduced. The burette is shaken at intervals for five minutes and then rinsed with fresh water introduced through the funnel tube, the pyrogallate being allowed to flow out of the lower stopcock. As soon as the walls of the burette are rinsed clean the bottom stopcock is closed and the volume read as before with the top stopcock open and the funnel tube filled with water.

Carbon monoxide is absorbed by acid cuprous chloride as usual (§ 6 of Chapter III), but a very considerable amount of preliminary manipulation is necessary. The alkaline pyrogallate must be thoroughly washed out by water flowing through the burette and then replaced by HCl sp. gr. 1.12. When this has been done the Cu_2Cl_2 reagent may be added and after the absorption the volume measured with the funnel tube filled with dilute HCl.

The only advantage which a burette of this type can claim is its portability. Its manipulation is cumbrous, the introduction of the large volumes of wash water changes the composition of the gas, and the temperature of the burette, which is usually not jacketed, is almost certain to change unless very unusual precautions are observed to keep it from contact with the hands of the operator and to have the temperature of the reagent and wash water the same as that of the room where the operation is being carried on. The Orsat apparatus is preferable for almost all purposes.

5. Chollar Tubes.—Mr. B. E. Chollar[1] in 1888 modified

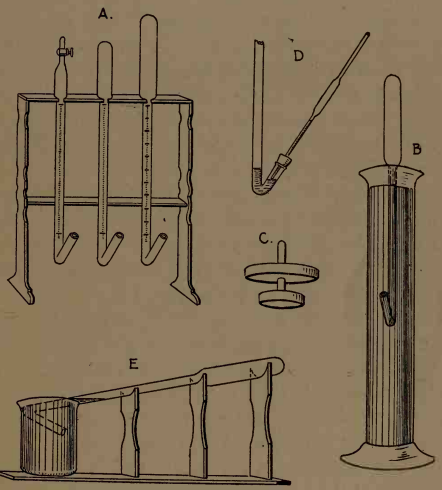

FIG. 18.—Chollar tubes for gas analysis.

Cooper's eudiometer and produced a very practical and simple combination burette and pipette. In Fig. 18 at A are seen three of the Chollar tubes in a rack. The zero point is the top of the bulb and the graduations start at the bottom of the bulb and extend down to the bend in the tube. The bulbed portion may

[1] *Proc. Western Gas Association*, 1893, 219.

occupy varying proportions of the total volume and since it is not graduated a tube must be chosen proportioned properly for the analysis to be made. Of the three burettes shown at A, that on the right is called a 10 per cent. burette because the graduations cover only 10 per cent. of the total volume. The middle burette is a 25 per cent. burette, and the burette on the left is a 50 per cent. burette, provided also with an upper stop-cock which is convenient, but not necessary for all the forms.

It is assumed that a plentiful supply of gas for analysis is available and that it is under pressure. A rubber tube is slipped into the burette round the bend and up to the top through which gas is blown until the air is displaced. It is safer to fill the tube with water and displace this with the gas. The rubber tube slips into the burette more readily if it is wet. When the burette is completely filled with gas it is immersed in the cylinder of water B far enough to seal the outlet and the rubber tube is withdrawn. The burette is now pressed completely under the water and kept there by the weighted cover C for a few minutes until the gas has attained the temperature of the water which should be at room temperature. The top of the burette is then grasped by the tip of the fingers to avoid warming the gas and the burette is raised until the meniscus inside of the burette coincides with the surface of the water in the glass cylinder when the gas volume is read at atmospheric pressure. In case the volume of the gas has increased through expansion so that the meniscus is below the graduations a portion of the gas must be removed by closing the lower end of the burette with the thumb while it is still under water and then by raising and tilting the burette causing a few bubbles to pass into the short arm from which they escape into the air when the thumb is removed.

To introduce reagents, a portion of the water is sucked from the short arm of the burette by a pipette as shown at D. Sufficient water must of course be left to seal the burette. Sufficient reagent such as caustic soda is then introduced to completely fill the short arm which is tightly closed by a rubber stopper or the thumb. The burette is then inverted and shaken until absorption is believed to be complete. The gas which may have gotten into the short arm is now worked back into the body of the burette by turning the burette almost horizontal and the

burette is again immersed in the large cylinder. The rubber stopper is removed after the outlet is sealed with water, water enters to replace the gas absorbed and the volume of the gas is read as at first.

The usual reagents for carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide may be used. A solution of arsenious oxide is recommended for hydrogen sulphide.

To wash out one reagent before adding another the burette is placed on the stand shown at E in Fig. 18 with its open arm pointing down in a beaker of water. The reagent being heavier than water tends to flow out. The washing may be accelerated by passing water into the burette through a rubber tube. The instrument is very readily portable and after a little experience results of considerable accuracy may be rapidly obtained.

CHAPTER VI

EXACT GAS ANALYSIS

1. Historical.—Lavoisier in his Traité Elementaire de Chemie published in 1789 devoted Chapter II of Book III to Gasometry or "The Measurement of Weight and Volume of Gaseous Substances." He described eudiometers, a gasometer of the bell jar type, and methods of separation of certain gases by absorption and explosion as well as the mathematical method of making correction for temperature and pressure.

Bunsen and Playfair[1] in a paper "On the Gases Evolved from Iron Furnaces" presented in 1845 what was perhaps the first serious attempt to develop methods of gas analysis for technical investigation. The methods published in this paper formed the basis of Bunsen's classic book "Gasometrische Methoden" published in 1857. Bunsen used a graduated cylindrical eudiometer inverted over a trough of mercury both for measuring the volume of the gas and for carrying out analysis by absorption and explosion. It was necessary to determine the temperature and pressure of the gas when each reading of volume was made and to make arithmetical corrections to bring the volume to standard conditions. It was possible to work accurately with his apparatus but it has been replaced by simpler forms which allow more rapid work.

Regnault and Reiset[2] in a paper on the respiration of animals developed a eudiometer which was capable of accurate work but was very cumbrous.

Doyere in 1848[3] exhibited before the French Academy of Sciences apparatus for gas exact analysis and two years later[4] presented details of the remarkably complete and ingenious apparatus which he had devised. He used a separate pipette

[1] *British Ass. for Advancement of Science,* 1845, 142.
[2] *Ann. de Chim. et de Phys.* (3), 26, 299 (1849).
[3] *Comptes rendus de l'Academic de Science,* Feb., 1848.
[4] *Annales de Chimie,* 3 Series, 28, 5, (1850).

for each reagent, measured his gases saturated with moisture instead of dry, and by means of a mechanical compensator avoided all corrections for change in gas volume due to temperature and pressure. He absorbed carbon dioxide by caustic potash and estimated oxygen by explosion or by absorption with ammoniacal cuprous chloride, two pipettes being used in series followed by a third containing dilute sulphuric acid. He also studied the estimation of hydrogen by explosion.

W. Hempel in the second edition of his Gas Analysis (1889) described a modification of Doyere's method in which he measured the gas volume in a bulb, varying the pressure of the gas at each reading so that its volume always filled the bulb to a definite mark. The pressure under which the gas stood was then measured and correction mathematically made to find the volume under standard conditions.

2. General Methods.—These earlier processes with their complications were necessitated by the imperfections of apparatus, especially stopcocks which could not be relied on to be gas-tight. With the development of reliable stopcocks came the development of apparatus so that now there is little need to use any of these older processes. The methods of exact gas analysis are now in general the same as those employed in technical analysis but with greater attention paid to the elimination of minor errors. The gas burette is graduated more accurately and an attempt is made to read to hundredths of a cubic centimeter instead of tenths. Correction is made either arithmetically or mechanically for variations in temperature and pressure of the gas during analysis. Mercury is used instead of water as the confining liquid in the burette and errors due to diffusion in the pipette are prevented. Special methods are sometimes introduced for the estimation of minute constituents of the gas.

3. Corrections for Temperature and Pressure.—According to the law of Boyle the volume of any gas varies inversely as the pressure and according to the law of Gay Lussac all gases expand under constant pressure by the same amount—about 1/273 of their volume—when heated from 0° C. to 1° C., and the same for each succeeding degree. The volume of a gas is almost universally expressed in scientific work as that which it would occupy

if completely dry and at a temperature of 0° C., and a pressure of 760 mm. of mercury. For technical purposes the gas is frequently calculated to the volume which it would have at 60° F. and 30 in. of mercury pressure when saturated with water. The formulæ for this calculation are given in § 4 of Chapter VII on the Heating Value of Gas.

The formula for the reduction of the volume of a dry gas to 0° and 760 mm. dry follows from the laws stated.

$$V_0 = \frac{V \quad p}{\left(1-\frac{t}{273}\right)760} \text{ or } V_0 = \frac{Vp}{(1-.00367t)760}$$

If the gas as measured was saturated with moisture at say 60° F. and it should actually be chilled to 0° C. most but not all of the water would be condensed. It is usual in calculations to assume either that the gas becomes completely dried which is the usual assumption or that the water all remains in the vapor state which is less frequently assumed. The formula given above will be the one used in the latter case where the water vapor is assumed to obey the gas laws without condensing, just as nitrogen or hydrogen would.

If the gas is to be reduced to standard conditions, dry, the volume of the water vapor must be deducted. Since the assumption is that the gas is saturated with moisture at the temperature "t" the proportion of moisture will be a constant which may be expressed either in terms of volume or more conveniently in terms of barometric pressure. Table I in the Appendix gives the vapor pressure of water, "a," for each 1° C. within the limits usually required. The formula for reduction of the volume of a gas read when saturated with moisture, to its volume when dry at 0° C. and 760 mm. is therefore as follows:

$$V_0 = \frac{V(p-a)}{(1-.00367t)760}$$

If the readings are in the Fahrenheit scale and in inches of barometric pressure the formula becomes

$$V_{32} = \frac{V(p-a)}{\left(1-\frac{t-32}{491}30\right)}$$

4. Description of Gas Burettes.—The burette for technical analysis does not allow an accuracy greater than 0.1 c.c. and the probable error is more nearly 0.2 c.c. The errors are in part due to the coarse graduations of the cylindrical burette tube and in part to liability to change in the temperature and pressure under which the gas volume is read. A device for automatically correcting for change in temperature and barometric pressure was devised by Petterson[1] in an apparatus for the analysis of air. This was quickly adapted by Hempel to his gas burette and as used by him consisted of a closed tube connected to one arm of a manometer whose other end connected with one tip of a three-way cock at the top of the burette. The volume of the gas instead of being read at a changeable atmospheric pressure was to be read at the unchanging pressure in the closed compensating tube. The modification of this type of apparatus developed by the author[2] is shown in Fig. 19.

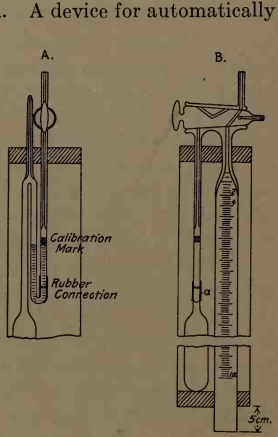

FIG. 19.—Details of gas burette with automatic compensator for temperature and pressure.

The burette has a specially bored stopcock as shown in the sketch which allows communication to be established through the stopcock between the burette and the compensating tube. The latter consists of a U tube manometer shown in A of Fig. 19 connected to the burette by a single rubber connection at *a*, placed so that gas never comes in contact with the rubber and there can be no possibility of leakage—a fault of the Hempel type of apparatus. The other end of the U tube bends down and terminates in a tube about the same diameter as the burette and

[1] *Zeit. anal. Chem.*, 25,467 (1886).
[2] *Jour. Am. Chem. Soc.*, 22, 343 (1900).

sealed at the bottom. At the top of the U is a capillary tip which in practice is fused shut as explained later.

In mounting the burette which is assumed to be clean and entirely taken apart the manometer is connected to the burette at *a* by a piece of good black rubber tubing wired in place, and the large rubber stopper at the lower end of the burette is pushed up until it rests snugly against the bottom of the comparison tube and presses the glass parts at *a* firmly together within the rubber tube. The glass water jacket tube is then slipped over the top of the burette and onto the lower rubber stopper and the upper split cork fitted into place. The burette is then placed in a stand such as is shown in Fig. 21. The levelling bottle is also connected to the burette as in technical analysis with the added precaution of wiring the rubber stopper into the burette so that it may not be blown out through the weight of the mercury column. The process of wiring in a rubber stopper is simple but since beginners are sometimes at a loss to accomplish it the following description is given. A piece of rubber tubing is first slipped over the bottom of the burette to give a soft surface for the wire to grip. A piece of copper wire about 18 gage is annealed by passing several times through the flame of a Bunsen burner and a piece about 4 in. long is twisted in the middle of one about 8 in. long to form a T. The longer piece is then bent around the burette and twisted till it fits snugly. Its two ends are now brought over the rubber stopper and twisted with the free end of the 4-in. piece of wire until the cork is firmly pressed in.

To prepare the comparison tube for use, a few drops of water are to be brought into its lower portion to saturate the air it contains, the manometer is to be filled with mercury and the capillary tip is to be fused shut. The two first operations can be conveniently accomplished in one operation. The burette is filled with mercury on whose surface are a few drops of water. By turning the stopcock to the position shown at D of Fig. 19, the water with the mercury following it may be passed through the stopcock and the U tube and over into the comparison tube. The progress of the mercury is to be arrested when the water has trickled down the comparison tube and the mercury is to be drawn back until there is just enough left in the U tube to fill it approximately to the calibration mark when there is atmospheric

pressure on both limbs of the U as shown in Fig. 19 at A. This may be readily accomplished after one or two trials. The capillary tip of the comparison tube is now to be sealed with a blow pipe and the burette is ready for use.

This burette has the advantage over the usual technical type that its readings are unaffected by variations in external temperature and pressure, but the volumes themselves cannot be read more accurately than with the technical type unless a reading telescope is employed. Even with this aid to the eye the results are not always certain for the presence of a few drops of water on the mercury alters the shape and boundaries of the meniscus.

5. The Bulbed Gas Burette for Exact Analysis.—The idea of converting the burette into a string of bulbs connected to a side arm burette apparently originated with Bleier.[1]

The author has utilized this suggestion in the design of the burette shown schematically in Fig. 20, and in perspective in Fig. 21; it consists of a burette with stopcock and manometer as already described. The main body of the burette contains twelve bulbs, each of a capacity approximating 12 c.c. A line is etched on each constriction and the capacity of the bulb between these marks is determined. Starting from the capillary above the top bulb a side arm springs, terminating in a small burette with total capacity of 15 c.c. and graduated in 0.1 c.c. Both these burette tubes connect at the bottom by means of heavy rubber tubes and a Y with a stopcock on each arm, to a common levelling bottle. A screw clamp on each rubber tube serves for the exact adjustment of the mercury. To measure a gas, the stopcock is placed in position shown at C of Fig. 19 and the mercury in the bulbed tube brought to the mark in one of the constricted portions by opening the proper stopcock on the Y and raising or lowering the levelling bottle. When adjusted, the mercury is held in its proper position by closing the stopcock on the Y. The stopcock leading to the small burette tube is then opened and the gas brought to approximately atmospheric pressure by proper change in the mercury level. The three-way stopcock at the top of the burette tube being now turned to position shown at D in Fig. 19, the burette is brought into connection with the manometer, which is properly set by further

[1] *Ber. d. Chem. Ges.*, 31, 1, 238.

changing the level of the mercury in the small burette. The final adjustment in both burettes is made by the screw clamps on the rubber tubes.

When the gas burette is used in the manner indicated the gas volume is read under conditions which are constant but not necessarily known. It is not usually necessary in gas analysis

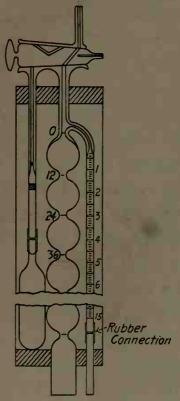

FIG. 20.—Details of bulbed gas burette for exact gas analysis.

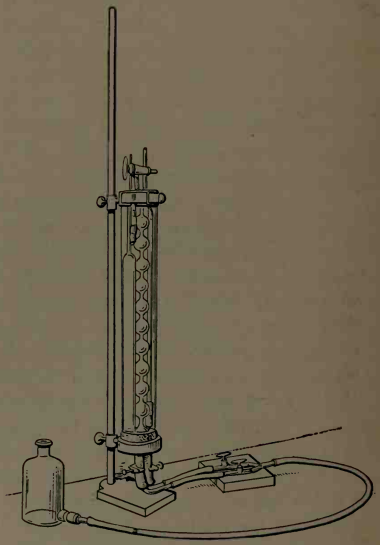

FIG. 21.—Burette for exact gas analysis.

to know the absolute value of a gas but it may be obtained if the temperature and barometric pressure are noted at the time the tip of the manometer tube is sealed. The volume of the gas is to be read when the level of the mercury in the two arms of the manometer is the same. The gas has then the same volume which it would have had at the temperature and pressure prevailing when the manometer was sealed. Correction to standard con-

ditions may be made mathematically as indicated in a preceding paragraph. This procedure for reading the gas volume is not as accurate as the one recommended for gas analysis where the mercury is brought tangent to the rim of a metal sleeve but it is amply accurate for most purposes.

6. Manipulation of Gas Burette for Exact Analysis.—It is necessary to discharge from the burette all of the residual gas including that in the manometer tube. This may be accomplished by discharging most of the gas from the burette into the air and then by turning the stopcock and lowering the levelling bottle, drawing into the burette the gas from the manometer until the mercury of the U tube is just at the stopcock. The gas in the burette may then be discharged into the air. If there is danger that alkali has been introduced into the burette in a previous operation it is advisable to draw into the burette a few cubic centimeters of acidulated water and with it rinse down the walls of the entire burette, subsequently expelling it. This also makes certain that the walls of the burette are wet so that the gas to be subsequently introduced will become saturated with water.

The gas is then introduced into the burette as in technical analysis. If a volume of approximately one hundred cubic centimeters are wanted, nine bulbs are filled with gas at atmospheric pressure. The stopcock at the top of the burette is then closed and the gas compressed into eight bulbs. Up to this time the side arm of the burette has remained filled with mercury. The stopcock on the Y is now opened and part of the gas transferred to the side arm until the whole is again under atmospheric pressure as shown by the agreement of the level of the mercury in the levelling bottle held in the hand of the operator, with the level of the mercury in the side arm. The stopcock on the Y is now to be closed and that at the top of the burette is to be turned to make communication with the manometer the mercury in which drops at once to approximately its proper position. By using the clamps on the rubber tubes as fine adjustments the meniscus in the bulbed tube is to be brought tangent to the mark between two bulbs and also the meniscus in the manometer is to be made tangent to the metal sleeve.

The volume of the gas will be read as x c.c. in the bulbs + y

c.c. in side burette + z c.c. in manometer. As there are these three readings to be made it is necessary that each be very accurate. Let us see how accurately this may be done. First, the mercury in the bulbed tube is to be brought to a specified mark in a tube of about 5 mm. internal diameter. By means of the screw clamp this may be done with such accuracy that the error is negligible. Second, the volume of gas in the side tube must be read. Each 0.1 c.c. in this tube occupies a space of a little over 2.5 mm. and it is possible to interpolate 0.01 c.c. with the eye with an error of less than 0.02 c.c. Third, the mercury in the manometer must be brought to a definite mark with such exactness that the barometric pressure, under which the gas volume is read, shall be almost identical each time. A difference of 1 mm. of mercury pressure changes the gas volume 0.13 per cent., which on a volume of 100 c.c. equals 0.13 c.c., an error far too large. It was found impracticable to attain the required accuracy when it was attempted to bring the mercury to a mark etched on the glass. The best device was found to be a band of thin, blackened copper, wrapped around the tube and cemented to the glass. It is possible to bring the mercury tangent to the lower surface of this with great exactness. In working with this burette the author is accustomed to make all readings in duplicate, readjusting at all points each time, and to repeat if the two differ from each other by more than 0.01 c.c. Duplicates usually agree within this limit. The greatest difficulty found in manipulation is to draw the liquid from the pipette over exactly to the burette stopcock and stop it there. If it gets into the burette, a bubble lodging in one of the capillary tubes frequently damps the sensitiveness of the manometer. If this happens the bubble may be shot out of its lodging place by compressing the rubber tube above the screw clamp with the fingers. Such a bubble may also be carried into the manometer, where it will obscure the surface of the meniscus. To remedy this it is well to keep 2 or 3 mm. of water on the surface of the mercury in the manometer. This allows a perfectly sharp reading of the mercury meniscus below the water-level. The manometer should respond to a very slight movement of the screw clamp.

The advantages of this burette may be summarized as follows: It is a compact burette which, without reading-telescope or other

accessories, allows the volume to be read with an error of less than 0.02 c.c., compensates automatically for changes of temperature and pressure, and avoids completely all errors due to inclusion of air or loss of gas in making connections with the absorption pipettes. The disadvantages so far developed are chiefly those inherent in all forms of apparatus which possess a stopcock and rubber connections. Both may leak; but on the other hand both may be kept so tight for limited periods of time as to introduce no measurable error.

7. Calibration of Burette.—The burette must be carefully calibrated throughout its entire length. This can best be done by weighing the mercury discharged. One cubic centimeter of mercury at 0° C. weighs 13.59 grm. Since all that is desired is a relative calibration the mercury need not be strictly pure nor need correction be made for its temperature. Ten milligrams of mercury corresponds to less than one-thousandth of a cubic centimeter so greater accuracy than this in weighing is a waste of time. Wire a stopper carrying a stopcock into the bulbed tube and fasten by a stiff rubber tube a stopcock to the side arm. It is especially important that the rubber tubing should not bulge under the mercury pressure and to prevent this it should be firmly wound with wire. Connect the tips of these stopcocks to the mercury levelling bottle and through them fill the burette with mercury completely to the stopcock. The portion first calibrated is the capillary tube from the bottom of the stopcock to the zero of the bulbed tube and the zero of the side arm. After that each bulb and each cubic centimeter of the side arm is separately calibrated. The accuracy of the calibration may be checked by the procedure of a regular analysis where a volume of gas is chosen such that it for instance fills 9 bulbs and a small portion of the side arm. The method of reading may then be changed to eight bulbs plus a considerable volume in the side arm but if the calibration is correct the same volume should, of course, be shown. The volume of the small portion of the manometer tube above the mercury may best be determined by filling the burette completely with mercury and then drawing the air out of the manometer tube into the side arm of the burette where it may be measured under atmospheric pressure with an error of a few tenths of a per

cent. Since the total volume is only a small fraction of a cubic centimeter the method is amply accurate.

8. Absorption Methods in Exact Gas Analysis —The same reagents may in general be used in exact as in technical analysis. Care should however be taken to see that the reagent has been recently saturated with gas of a sort similar to that which is to be analyzed. In case the reagent is one which does not attack mercury the pipette is to be filled with mercury which carries on its surface only a few cubic centimeters of the reagent. If pipettes of the ordinary type are filled with mercury the mercury rising in the second bulb places the gas under considerable pressure and greatly increases the danger of leakage at the rubber connections. An explosion pipette may with advantage be used as an absorption pipette under these circumstances since its stopcock and levelling bottle allow a regulation of the pressure within the pipette. Where the greatest accuracy is not required it is sufficient to lessen the errors due to diffusion by introducing a few cubic centimeters of mercury to form a seal in the ordinary form of pipette. In the case of solutions like cuprous chloride where mercury cannot be used reliance must be placed on the complete saturation of the reagent. Where gases are readily soluble errors due to diffusion mount up rapidly. For instance: A sample of 74 c.c. of acetylene gas when passed into an ordinary KOH pipette as used in technical gas analysis decreased to 63.9 after quietly standing for three minutes, to 58.0 after a second contact, and to 29.0 c.c. after three minutes shaking with the same reagent. After two more similar periods the residue left in the burette was only 5.2 c.c. A second sample of gas behaved similarly, and by connecting a burette with the second bulb of the pipette the acetylene diffusing through was recovered quantitatively.

9. Carbon Dioxide.—Carbon dioxide is usually estimated by absorption in caustic soda as in technical analysis. If other acid gases such as H_2S, SO_2, or HCl are present they may be removed by first shaking the gas in a pipette containing $KMnO_4$ very faintly acidified with H_2SO_4. An increase in volume after this operation would indicate that oxygen had been evolved during the process. If direct evidence of the presence of CO_2 is desired a clear solution of $Ba(OH)_2$ should be used instead of NaOH in the pipette for CO_2 absorption. The formation of a

white precipitate completely soluble in HCl will show the presence of carbonates.

10. Unsaturated Hydrocarbons.—Unsaturated hydrocarbons as a class are estimated as in technical gas analysis by absorption with fuming sulphuric acid or bromine water. It is difficult to prevent the errors due to diffusion mentioned in § 8 since both reagents attack mercury. Where it is desirable to eliminate the error as far as possible a stopcock may be placed in the line between the two bulbs of the pipette which can be closed after the gas has been passed into the pipette while absorption is taking place.

A separation of the constituent unsaturated hydrocarbons is rarely carried out. It is best accomplished by bubbling a known volume of the gas through bromine and fractionating the resulting bromides. The results are at best unsatisfactory. Ernshaw[1] has shown that it is possible to calculate the average composition of the illuminants from data obtained by exploding a sample of the gas which still contains the olefines and deducting from the observed contraction and carbon dioxide the amounts due to hydrogen, carbon monoxide and the paraffines. The method demands very accurate work.

Acetylene may be absorbed in a faintly ammoniacal solution of silver or copper salts. The precipitated acetylides are explosive when dried and care should be taken in handling them. The ammonia vapors are to be removed from the gas by shaking with dilute acid before the volume is measured. Water dissolves more than its own volume of acetylene, so great care must be exercised to saturate the water of containing vessels before the gas to be analyzed is brought into them. Also gas from which large percentages of acetylene have been removed must not be returned to vessels containing much water with which it had previously been in equilibrium since the water will give back to the gas material amounts of acetylene.

Phosphorus forms a delicate reagent for qualitative detection of traces of unsaturated hydrocarbons. If when the gas in question is brought in contact with phosphorus under the conditions prescribed for the estimation of oxygen, white fumes form, it is certain evidence of the absence of more than minute traces of unsaturated hydrocarbons. If on the other hand the

[1] *Jour. Franklin Inst.*, 146, 161 (1898).

fumes fail to appear even after the addition of air it is not absolutely certain that the inhibiting catalyzer is an unsaturated hydrocarbon for ether, chloroform and a number of other substances behave similarly.

11. Oxygen.—The estimation of oxygen by phosphorus as in technical analysis admits of little improvement in simplicity or accuracy. Alkaline pyrogallate may be used where it is not possible to remove the inhibiting catalyzers which prevent the use of phosphorus.

12. Carbon Monoxide.—It was stated in Chapter II that the methods for estimation of carbon monoxide were unsatisfactory. They are more unsatisfactory for exact than for technical analysis. The absorption by cuprous chloride given in technical methods is hardly to be considered as an accurate method. The change in the absorption spectrum of blood after treatment with carbon monoxide may be made an accurate qualitative test for carbon monoxide but does not lend itself readily to quantitative purposes.

The method usually employed is to oxidize the carbon monoxide, after having made certain that all other compounds which would be affected by the oxidizing agent have been removed.

Iodine pentoxide is the most commonly employed oxidizing agent, the reaction being:

$$I_2O_5 + 5CO = I_2 + 5CO_2$$

The especial value of this reaction lies in the ease with which the iodine formed may be estimated, it being the iodine and not the carbon dioxide which is used to measure the amount of carbon monoxide. The details here given are essentially those of Kinnicutt and Sanford,[1] who used substantially the method of Nicloux. The gas is first purified by being bubbled slowly through concentrated sulphuric acid and then passed through a tube containing lumps of caustic soda. This treatment removes unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide and similar reducing gases. The purified gas is then passed through iodine pentoxide contained in a U tube immersed in an oil bath at 150° C. Following the U tube comes another absorption tube containing about 0.5 g potassium iodide dissolved

[1] *Jour. Am. Chem. Soc.*, 22, 15 (1900).

in 10 c.c. of water. If a liter of gas is used as small an amount as 0.025 c.c. of carbon monoxide may be detected. The method is ordinarily only used for the detection of minute amounts of carbon monoxide and it is not suitable for large amounts. The absence of any liberated iodine may be considered a positive proof of the absence of carbon monoxide. The liberation of iodine is however only a proof that some reducing substance was present, which can only with certainty be claimed as carbon monoxide after careful blank tests have shown that the purifying train is adequate to remove all other reducing substances and that the iodine pentoxide does not yield iodine except in the presence of such a reducing substance.

Gill and Bartlett[1] tested this method on illuminating gas and report results about nine per cent. high. They report accurate results when mixtures of carbon monoxide and air are used.

13. Hydrogen.—Hydrogen may be directly absorbed in metallic palladium but is almost always oxidized. The gas should first be freed from unsaturated hydrocarbons and other reducing gases as well as oxygen, so that it contains only hydrogen, saturated hydrocarbons and nitrogen. There is then a choice of methods—one class oxidizing the hydrogen without affecting the hydrocarbons, and the other simultaneously oxidizing both hydrogen and hydrocarbons.

There are several methods for fractional oxidation of hydrogen which are reliable. The errors which attend the method of simultaneous oxidation of hydrogen and methane have been briefly discussed in Chapter IV. The important systematic error in explosions and flame combustions is due to the oxidation of nitrogen. The formation of oxides of nitrogen increases with higher temperatures. The most favorable mixture for their formation is one in which there are equal volumes of oxygen and nitrogen. The errors are therefore minimised by keeping the temperature of combustion low and by making the diluting gas as nearly pure oxygen as possible. It is not possible to give an absolute statement of the magnitude of the error introduced for it will vary with each difference in the form of the explosion vessel and in the violence of the explosion. The following

[1] *Jour. Ind. and Eng. Chem.*, 2, 9 (1910).

series of measurements by the author[1] will indicate the magnitude of the error and also the accuracy of the burette for exact gas analysis described in this chapter.

EXPLOSION OF PURE HYDROGEN

Hydrogen, c.c.	Air, c.c.	Contraction after explosion, c.c.	Calculated per cent. hydrogen	Contraction over potassium hydroxide, c.c.	Explosive ratio
11.35	84.80	16.90	99.26	0.00	4.64
12.11	85.57	18.08	99.53	0.00	4.37
14.19	84.27	21.27	99.92	0.00	3.62
16.77	85.77	25.13	99.90	0.01	3.06
16.54	82.64	24.76	99.80	0.01	3.00
18.19	83.22	27.29	100.01	0.01	2.71
21.10	83.28	31.74	100.28	0.00	2.29
27.04	83.86	40.80	100.59	0.11	1.73

The hydrogen was prepared by the action of caustic potash on aluminium so as to be free from hydrocarbons. It will be noted that in this series air was used to supply the oxygen and as the diluent. A variation of 1.3 per cent. in the purity of hydrogen due solely to errors inherent in the explosion process make it evident that the method can hardly be called an accurate one.

The errors attendant upon the flame combustion method of Dennis and Hopkins described in § 9 of Chapter IV are illustrated in the following series.

COMPARISON OF EXPLOSION AND COMBUSTION METHODS ON HYDROGEN

Explosions with Air

Sample hydrogen c.c.	Air c.c.	Contraction after explosion, c.c.	Contraction over potassium hydroxide, c.c.	Hydrogen per cent.	Explosive ratio
15.32	85.34	22.71	0.04	98.82	3.43
18.15	82.39	26.93	0.06	98.91	2.73

Explosions with Oxygen

	Oxygen				
14.82	93.51	22.04	0.02	99.14	3.91
16.48	82.18	24.51	0.02	99.15	3.02
20.58	80.09	30.60	0.03	99.12	2.29

[1] *Jour. Am. Chem. Soc.*, 23, 476 (1901).

Combustions by the Dennis and Hopkins Method

Hydrogen c.c.	Oxygen c.c.	Air c.c.	Contraction after explosion, c.c.	Contraction over potassium hydroxide, c.c.	Hydrogen per cent.	Oxygen in excess
91.29	51.65	54.55	136.72	0.04	99.84	13.72
58.48	53.39	50.14	87.43	0.10	99.66	40.89
89.31	40.77	50.21	133.57	0.07	99.70	3.73

The values obtained by explosion with oxygen are remarkably concordant and are probably as accurate as we can hope to attain. The values obtained by explosion with air are higher and more irregular. The values of the Dennis and Hopkins method are also high and involve an error of about 0.6 per cent.

14. Methane.—There are no absorption methods for methane which are acceptable. It is estimated by oxidation to CO_2 and H_2O with measurement of the change in volume after oxidation and after absorption of the CO_2. The general methods are given in § 7 to 11 of Chapter IV. There is greater liability of error in the explosion process through formation of oxides of nitrogen than is the case with hydrogen, as is illustrated by the following series of tests of methane made from methyl iodide and the zinc copper couple.

EXPLOSION OF METHANE

Sample methane c.c.	Air c.c.	Contraction after explosion	Carbon dioxide c.c.	Methane per cent.	Hydrogen per cent.	Explosive ratio	Ratio contraction / sample
7.05	92.07	13.09	6.53	92.62	0.28	4.05	1.85
8.93	104.17	16.66	8.31	93.28	0.14	3.53	1.86
9.07	98.35	17.10	8.54	94.15	0.14	3.19	1.88
10.20	98.22	19.27	9.63	94.41	0.06	2.61	1.89

In these experiments the explosive ratios all lie within the limits set by Bunsen. Still there is a variation of 1.6 per cent. in the apparent percentage of methane as calculated by the usual methods and a corresponding variation in the amount of hydrogen. Similar experiments made with commercial oxygen (96.5 per cent. pure) as the diluting agent instead of air showed errors rather greater than when using air in similar amount. The greater error in analyzing methane as compared with hydrogen

results almost certainly from the higher temperatures attained in the explosion of methane. It is not possible to dilute the gas sufficiently to avoid this danger without running the risk of incomplete combustion of the methane. The methods of oxidation of methane which involve flame as in explosion or the Dennis and Hopkins method cannot be considered very accurate. Jaeger's method of analysis by combustion with copper oxide in a combustion tube as described in § 11 of Chapter IV cannot involve the formation of material amounts of oxides of nitrogen. This method is not so rapid or convenient as the others but, if care is taken to carefully cool the gas including that remaining in the combustion tube to its initial temperature before noting the change in volume, it is believed to be the most accurate method.

15. Nitrogen.—The method of removal of all gases except nitrogen by combustion with copper oxide as given in § 12 of Chapter IV is fairly exact. The gases of the argon group are left with the nitrogen but the separation of these is not included in this work.

CHAPTER VII

HEATING VALUE OF GAS

1. Introduction.—The heating value of gases may be determined by combustion in a bomb calorimeter but the difficulty of transferring a definite quantity of gas to the bomb prevents the general adoption of such a method. The standard type of calorimeter is one in which the gas is burned with atmospheric air and the total heat of the products of combustion is as completely as possible transferred to the water of the calorimeter. A continuous flow calorimeter is usually employed wherever a sufficient amount of gas is available, but the intermittent type is also used. In some other types of calorimeter the heat of combustion is used to raise the temperature of a piece of metal, or a thermocouple placed in the flame. Calorimeters of these latter types give merely relative figures which can only be converted into heat values after very careful calibration. They are in no sense standard instruments and are not discussed in this book. It is also possible to calculate the heating value of the gas from its chemical composition with approximate accuracy.

2. Continuous Flow Calorimeters.—The continuous flow calorimeter bears much resemblance to the type of instantaneous water heaters found in bath rooms. The gas after passing through a meter, is burned in a Bunsen burner. The products of combustion give up their heat to a stream of cold water flowing in a direction opposite to that of the gases so that the gases emerge from the instrument cold and the water emerges hot.

The process to be accurate requires the fulfillment of the following conditions:

a. The gases must be accurately measured, be burned at a constant rate, and combustion must be complete.

b. The water must enter at a constant rate and at constant temperature, and be at approximately room temperature.

c. The heat of combustion must all be transmitted to the

water whose mass and rise in temperature must be accurately determined.

The pioneer calorimeter of this type was that devised by Hugo Junkers in 1893.[1] It is an excellent and widely used instrument which has in recent years had several imitators. It will be described in detail after a discussion of the general principles.

3. Wet Gas Meters.—The gas is usually measured in a wet meter which consists of a horizontal cylindrical casing of sheet metal enclosing a horizontal drum and filled about half full of water. The drum is divided with slant partitions into three or four compartments, each with its own entrance for gas at the back and its exit at the front. Each of these compartments constitutes a distorted screw thread enlarged to a chamber in the center. As the inlet of one of these compartments comes out of the water the pressure of the gas entering causes the drum to revolve and the compartment fills with gas. When the compartment is full the inlet dips below the water and seals, the outlet unseals and the water entering the compartment drives out the gas before it. If there were only one or two compartments the flow of gas could not be continuous, but with three or four compartments in the drum, one is always discharging and the rate of flow of gas is about constant.

It will readily be seen that the capacity of each compartment and the time of sealing and unsealing the inlet and outlet will be affected by the height of water in the meter so that the exact setting of the water level becomes of great importance. Each meter is provided with a gage glass and a pointer which can be adjusted to indicate the proper water level. The Committee on Calorimetry of the American Gas Institute in its 1912 report states that even with careful work an error of 0.3 per cent. may be introduced by inaccurate adjustment of the water level and that on passing 100 cubic feet of gas through the meter an error of about equal magnitude may be introduced through evaporation of the water. The meter must be calibrated frequently for accurate work.

Although it may be desirable to use the imported Junkers calorimeter, there is no similar reason for using the German meter

[1] *Jour. fur Gasbel.*, 36, 81 (1893).

which reads in the metric system. An American meter passing 0.1 cu. ft. per revolution is much more convenient.

The gas meter must be calibrated by passing through it a known volume of gas. This known volume may most accurately be obtained by the use of what is known as a cubic foot bottle or a smaller container of the same type. Containers of this type should be rigidly made of glass or metal and tapered at the top and bottom to glass tubes of small diameter upon which zero marks are etched. The capacity of one of these containers is determined by the weight of water which it contains. They may be bought in elaborate forms and with the certificate of the Bureau of Standards. Where a standardized bottle is not available a sufficiently accurate substitute may be improvised from a gas holder of the type shown in Fig. 24. This consists of a cylinder of galvanized iron coned and terminated with a cock at both ends. If this is filled with water at room temperature and weighed, and then drained and weighed, the volume of the tank may be calculated from the following table. The volume thus obtained may be considered constant within ordinary ranges of temperature since the coefficient of expansion of mild steel is only 0.0000067 per degree Fahrenheit.

The tank shown in the illustration holds one-third of a cubic foot and is weighed upon the balance shown in front of it. If larger tanks are used they must be made of heavy material so as not to change in volume when filled with water.

WEIGHT OF ONE CUBIC FOOT OF WATER

50° F.	62.41 lb.
60° F.	62.37 lb.
70° F.	62.31 lb.
80° F.	62.23 lb.
90° F.	62.13 lb.

In making the test the tank is to be filled absolutely full of water of almost room temperature and left standing by the side of the meter in a room of fairly constant temperature for several hours to make sure that all the parts of the system are at the same temperature. The gas supply is to be bubbled through water in order to be certain that it is saturated with water vapor.

If the depth of water in the saturator is so adjusted that no gas bubbles through unless a very slight suction is applied, it will obviate mathematical corrections, because if the static pressure of the water in the saturator is adjusted to counterbalance the pressure of the incoming gas, and the outlet of the discharge from the tank is set at the level of the lower cock, a direct comparison of the volume of gas registered by the meter and the capacity of the tank gives the calibration factor for the meter without any calculation for difference in pressure. So long as the whole system is at the same temperature it is immaterial what the temperature is. The upper cock of the tank may now be connected directly to the outlet of the meter. The lower cock of the tank should have a rubber tube attached which drops down to allow the formation of a water seal and rises again to discharge the water at the level of the cock. If now the lower cock on the tank is opened water will flow out through the rubber tube and an equal volume of gas will flow through the meter. When the water is all out of the tank the gas will be automatically stopped by the water seal in the rubber outlet tube and the whole system will be under atmospheric pressure, which is a condition necessary for accurate work.

4. Corrections for Temperature and Pressure.—The volume of the gas used in a test must be corrected for temperature and pressure. The standard conditions for the United States and Great Britain are a temperature of 60° F. and a barometric pressure of 30 in. of mercury. The gas as it comes from the wet meter is assumed to be saturated with water and correction is made for the excess of water vapor over that normal for 60°. Tables giving the correction factors in convenient form have been issued by the Gas Referees of London. They are derived according to the formula.

$$n = \frac{17.64(h-a)}{460+t}$$

where n = factor sought
h = height of barometric column in inches mercury
a = vapor tension in inches of mercury at temp. t
t = observed temp. of meter in degrees F.

Although this formula apparently involves the full correction for vapor tension which would reduce the volume of gas to a dry basis at 60° F., there is a further correction contained in the figure 17.64 of the formula which corrects the gas to a basis of 60° F. when saturated with water. The full formula is as follows:

$$n = \left(\frac{1}{1+\frac{t-32}{491}}\right)\left(1+\frac{60-32}{491}\right)\left(\frac{h-a}{30}\right)\left(\frac{30}{30-.51}\right)$$

The first member of the formula corrects the volume to 32° F., the second to 60° F., the third to dry gas under 30 in. barometric pressure, and the fourth to gas saturated with moisture at 60° F. the 0.51 being the vapor pressure of water at 60 ° F. Table III in the Appendix gives the factors for each degree Fahrenheit and each 0.1 in. pressure within wide limits.

5. Control of the Water.—The water supply must always be sufficient to keep the overflow on the small elevated constant-level tank in operation. If the supply of water to the tank slackens much the rate of flow to the calorimeter will also change. The temperature of the water should also be constant and approximately that of the room. In order to insure a water supply or even temperature and pressure it is advisable to install in the calorimeter room an elevated tank of at least 20 gallons capacity connected to the water mains and provided with an overflow from which the supply for the calorimeter is drawn.

6. Measurement of Temperature.—The temperature of the inflowing and outgoing water is determined by thermometers which should read to tenths of a degree. They must be carefully calibrated throughout their length by comparison with a standard. It is immaterial whether they are Centigrade or Fahrenheit thermometers but the Fahrenheit are more convenient, when as is customary, the results are to be expressed in British thermal units per cubic foot of gas. The thermometers are to be carefully placed in the calorimeter so that their bulbs are completeiy surrounded by water and are nowhere in contact with the metal of the calorimeter.

7. Measurement of Mass of Water.—The mass of water heated during an experiment may be determined either by measurement or by weight. A 2000-c.c. graduated cylinder is fre-

quently used. This is not an ideal device, for not only are the graduations coarse but the varying temperatures at which the water is measured necessitate the use of different correction factors to reduce the volumes to the equivalent weights. It is much more satisfactory to weigh the water. If the thermometers are in the Fahrenheit scale it is more convenient that the balance shall weigh in pounds and hundredths of a pound. If the thermometers read in the Centigrade scale it is more convenient to preserve the metric unit throughout. The water should be weighed in a metal bucket or glass vessel for which a counterpoise is provided. It is convenient to counterpoise the bucket with the interior wet as it is just after the water has been poured out after a test. Its weight will be so nearly constant that it is not necessary to counterpoise after each test. The balance should be capable of carrying ten pounds on each pan with a sensitiveness of one-hundredth of a pound.

8. Junkers' Calorimeter.—The original form of Junkers' gas calorimeter is shown in Fig. 22 and the improved form in Fig. 23. The Committee on Calorimetry of the American Gas Institute suggested that the older type of Junkers' calorimeter would be improved if the inlet and outlet thermometers were brought to the same level so as to facilitate rapid reading of the two. This change has been effected in the improved instrument but it is claimed by some observers that the efficiency of the newer type is not so high as the older. The numbers and letters refer to the same parts in each figure and the same description will answer for both of these instruments as well as for others of the same type put out by other manufacturers. The gas coming from the meter is burned in a Bunsen burner placed in the cylindrical combustion chamber of the instrument. The hot gases rise in the central chamber, pass down through a series of small tubes in the annular water jacket surrounding the combustion chamber, unite again in a single flue at the bottom of the instrument and pass out through an orifice whose size may be regulated by a damper. Water enters through the rubber tube w to the small elevated tank a which serves to supply water to the calorimeter under a constant head. The amount of water flowing into the instrument is controlled by the valve b and the waste water from a is discharged at c. The water traversing the instru-

ment passes out at *d* and during the actual test is measured in the graduated cylinder shown, or collected in a vessel and subsequently weighed.

The operation of the instrument is shown in detail in Figs. 22 and 23. The sectional illustration shows the burner (2) prop-

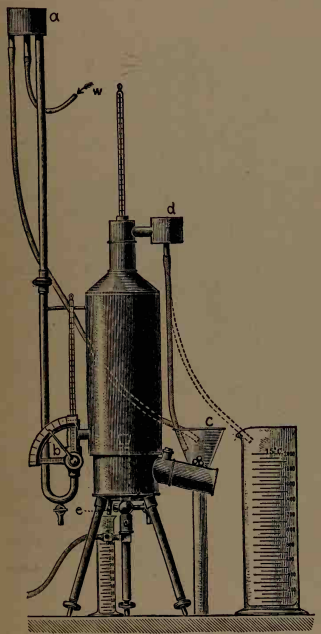

FIG. 22a.—Junkers' gas calorimeter. Original form.

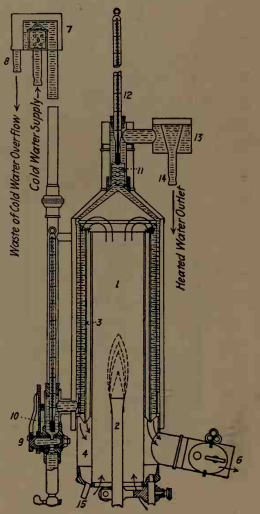

FIG. 22b.—Section of Junkers' gas calorimeter. Original form.

erly placed in the combustion chamber (1) and the path of the combustion gases and the water. The products of combustion rise in the central chamber, turn at the top, descend the annular cooling chamber (3) to the drum (4) pass the thermometer (5) and escape at (6). The water rises to the small overflow cup (7)

traversing a filter of wire gauze. The excess of water overflows and passes out of the instrument to the waste pipe through a rubber tube attached at (8). The small vessel (7) must always be kept overflowing to insure a constant pressure and hence a

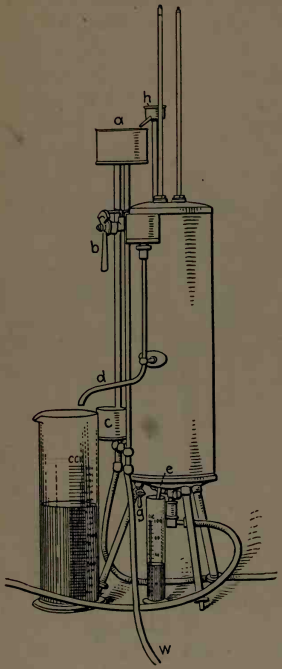

FIG. 23a.—Junkers' improved gas calorimeter.

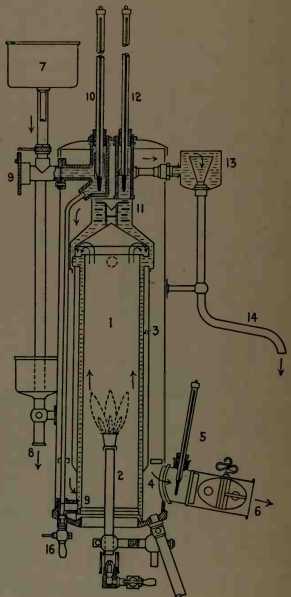

FIG. 23b.—Section of Junkers' improved gas calorimeter.

constant supply of water through the valve (9). The water passes the thermometer (10) which registers the inlet temperature and in the newer form of instrument descends in a small pipe within the outer casing to the bottom of the instrument. In both forms of instrument the water rises in the annular chamber

surrounding the gas passages (3), thus passing in a direction opposite to that of the combustion gases. The water from the annular chamber passes through the drum (11) provided with baffle plates to mix it and insure that all parts of the stream are of uniform temperature, passes the thermometer (12) which registers the outlet temperature, to the overflow vessel (13) and out at (14).

The water formed in the combustion of the hydrogen and hydrocarbons of the gas is condensed as it descends the annular condenser (3) and passes out of the drip shown at (15) and at *e* and is caught in a graduated cylinder. The working parts of the calorimeter thus described are insulated from the room by an air jacket. The outer casing of the calorimeter is nickel-plated and to be kept polished to lessen the loss of heat by radiation. It is well to drain the calorimeter when not in use by opening the cock (16). There is some danger that air brought in by the incoming water may collect around the inlet thermometer and disturb the accuracy of its readings. In the improved form, the tube (h) shown at the top of the calorimeter in Fig. 23 is to allow such bubbles to escape. Any water entrained by the bubbles passes out of the small overflow.

9. Preliminaries of a Test.—The calorimeter is to be set up on a table where the light is good, where there are no draughts, and where there is a water supply and a waste pipe. Fig. 24 shows the calorimeter set in a hood which has been modified by lowering a portion of the floor to bring the thermometer more nearly on a level with the eye of the observer. On the top of the hood is a zinc-lined wooden tank connected to the water supply and provided with an overflow pipe, from which the water supply for the calorimeter is drawn. This large overflow tank is advisable as it compensates for variations in the temperature and pressure of the city water supply.

The first step is to turn on the water and regulate the supply so that it flows through the instrument at the rate of approximately 1.5 to 2.0 liters per minute in case illuminating gas of ordinary quality is to be tested. The water must continuously overflow from both cups (13) and (8) of Figs. 22b and 23b. No water should drip from spout (15) nor from any other part of the instrument.

The gas meter is to be levelled and more water added if necessary to bring the bottom of the meniscus of the water on a level with the pointer. This is to be done when there is no gas pressure on the meter, and to ensure this state of affairs the burner cock on the outlet of the meter should be open and an opening should be made to the air on the inlet side of the meter. This may usually be most conveniently effected by disconnecting the rubber tube, but may also be accomplished by unscrewing the small plug at the bottom of the well below the gas inlet. This also

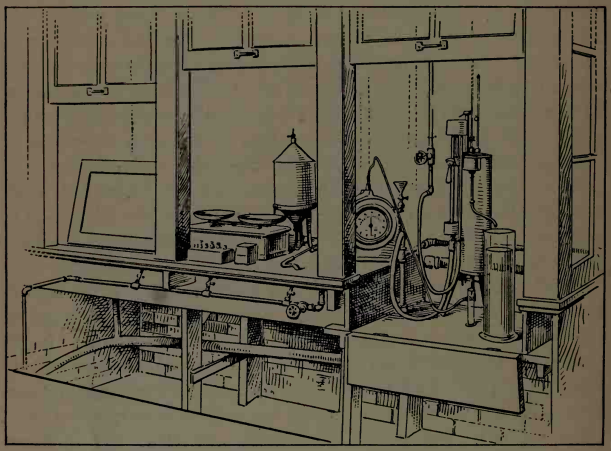

FIG. 24.—Gas calorimeter and accessories.

serves the purpose of removing any water which may have spattered into the gas inlet. The probable error in adjusting the water level is 0.3 per cent. so that when a greater accuracy is required the meter should be recalibrated after adjustment. The gas supply is to be connected to the meter and then to the calorimeter. A pressure regulator should be unnecessary on a city gas supply if the meter works smoothly. Directions are frequently given to interpose a regulator of the floating bell-jar type between the meter and the calorimeter. If this is done

it must be watched closely because any variation in the heights of the drum of the regulator at the beginning and end of the test causes an error in the measurement of the gas. Long connections of rubber tubing are to be avoided since rubber is porous and also exerts a selective solvent action on the hydrocarbons of the gas. The connections should be of glass with short lengths of rubber on each end.

The system is to be tested for leaks by closing the burner cock and opening the inlet cock on the gas main. The large hand of the meter should not show any perceptible change in position after two minutes. When the system has been found to be tight the burner cock may be opened and the gas allowed to escape into the air of the room until the large hand of the meter has made one complete revolution. It may then be lighted without danger of explosion unless the gas is acetylene, uncarburetted water gas or similar gases having wide explosive limits. Be sure that no unburned gas gets into the calorimeter where it might cause explosion later.

The flame from the burner is to be regulated so that it is a clear blue color with just a tinge of yellow at the tip. The volume will depend on the quality of the gas. Special tips for gases of very high or low heating value are provided with the instrument. With ordinary illuminating gas the rate of flow should be between 5 and 7 ft. per hour. The gas should be burned with a small excess of air. The draft may be controlled by the butterfly valve (6) of Figs. 22 and 23. The valve should be set to give maximum readings of the thermometer on the water outlet. That setting which gives the highest result is the most accurate. The flame must burn perfectly steadily. If it flickers the most probable cause is the presence of water in some of the connections. The rubber tubing should be disconnected and drained, the plug in the well below the inlet of the meter removed, and the pressure regulator examined. It may be that the flickering is due to friction within the meter which causes the drum to stick. This can usually be observed by closely watching the large hand of the meter and observing if it lags at particular points of its revolution. Trouble from this source cannot usually be remedied without sending the meter back to the factory. Flickering of the flame of the test burner may also be due

to fluctuations in the pressure of the gas in the mains or services. A U-gage attached to a gas outlet will show whether this is the case. If it is necessary to test gas under these conditions the flickering may be lessened by interposing between the gas outlet and the meter a large empty bottle. Care must be taken to fill this bottle completely with water and then displace this with gas to avoid danger of explosion.

If the meter has been recently filled with fresh water the gas should be allowed to burn for an hour before the test in order that the water of the meter may become saturated and not cause any change in the composition of the gas passing through it.

10. Description of a Test.—When the gas and water supply and the burner have been thus adjusted, the lighted burner may be placed in the calorimeter, care being taken to properly center it. This operation is facilitated by a small mirror placed below the instrument. The thermometer in the outlet water will at once commence to rise, and in a few minutes will be constant to within a few tenths of a degree. The increase in temperature of the outflowing over the incoming water should not be more than 10° C. and it may be necessary to readjust the water and gas supply to obtain this condition. If it is necessary to change the adjustment of the gas the burner should be removed from the calorimeter. The butterfly valve must not be closed enough to prevent the flame from burning strongly and freely. The escaping gases should not have any odor of unburned gas. Their temperature should be only a few degrees above that of the water entering.

The water formed in the combustion of the hydrogen and hydrocarbons will condense in the calorimeter and commence to drip from the small spout at the bottom of the instrument. The test should not be commenced until the thermometer on the water outlet has remained constant for several minutes and the condensed water has also commenced to drip from its spout showing that equilibrium has been reached within the calorimeter.

The counterpoised bucket for the water is placed in a convenient position and as the large hand of the meter passes a zero mark the water is turned into the bucket. Both thermometers are now to be read at each quarter position of the meter hands or more frequently. The outlet thermometer sometimes fluctuates

rapidly and it is well under such circumstances to read it as many times as possible so as to obtain a fairer average. A consumption of 0.2 of a cubic foot, or two revolutions of the large meter hand is sufficient with illuminating gas. The last thermometer readings will be made when the meter hand is in the three-quarter position. The operator then watches the meter while holding one hand on the tube through which the outlet water is flowing and as the meter hand again reaches the zero he swings the tube out of the bucket, thus marking the completion of the test. After the water has been weighed a duplicate test may at once be started. The procedure is the same in case the water is to be measured in a graduated cylinder instead of being weighed. The volume readings of the cylinder must be converted into grams by means of the table in § 6 of Chapter XVI on Manipulation of the Bomb Calorimeter. It is not possible to read the volume very accurately in a wide graduated cylinder.

The water of condensation dripping from the instrument is to be measured to allow the calculation of the net heating value. It is accurate enough to catch the water formed from 1 cu. ft. in a 50 c.c. graduated cylinder.

In case the temperature readings have not stayed constant within a few tenths of a degree during the test, the results should be discarded and an attempt be made to better the conditions.

If for any reason the burner goes out during a test and unburned gas gets into the instrument, it must be expelled before again lighting the flame. This may readily be accomplished by blowing vigorously through the escape pipe of the combustion gases.

11. Calculation of Results.—The heating value of gas is usually expressed, in English speaking countries, in British thermal units per cubic foot of gas measured when saturated with moisture at 60° F. and under a barometric pressure of 30 in. of mercury. The method for correcting the observed volume of gas to these standard conditions has been described in § 3. The factors for converting cubic centimeters of water at various temperatures to grams are given in § 6 of Chapter XVI. A Calory is accurately enough defined as the amount of heat required to heat 1 kg. of water 1° C., and a British thermal unit to be the amount required to heat 1 lb. of water 1° F. irrespective of the

absolute temperature of the water. The formula for calculation of the heating value is

$$HV = \frac{m(t' - t)}{v}$$

where m = mass of water heated
t′ = mean temperature of water flowing out
t = mean temperature of water flowing in
v = corrected volume of gas burned

If m is expressed in pounds, t in degrees Fahrenheit and v in cubic feet, the result is at once British thermal units per cubic foot.

If m is expressed in kilograms, t in degrees Centigrade and v in cubic feet, the result is in the hybrid unit Calories per cubic foot which may be corrected to British thermal units per cubic foot by multiplying by 3.968.

If m is expressed in grams, t in degrees Centigrade and v in liters the result will be in the metric unit, small calories per liter which is the same as Calories per cubic meter. This is the method of reporting heat values in Germany and other countries which use the metric system. To convert Calories per meter to British thermal units per cubic foot of gas measured under the same condition multiply by .1124. In scientific work the heating value of a gas is usually reported as Calories per cubic meter of dry gas at 0° C. and 760 millimeters pressure. In technical work in Germany the gas volumes are usually corrected to 15° C. and 760 mm. pressure which makes the conditions practically the same as prevail in this country.

The following calculations are for a test where an American meter passing 0.1 cu. ft. per revolution and provided with a Fahrenheit thermometer was used, while the calorimeter thermometers were of the metric system and the water was weighed in kilograms.

Meter reading at start	21.200
Meter reading at close	21.400
Meter temp.	71° F.
Barometer	29.8
Correction factor for temperature and pressure	0.965
Correction factor for meter	0.996

Temperature of water	
In	Out
12.1° C.	21.5° C.
12.1° C.	21.5° C.
12.2° C.	21.5° C.
12.2° C.	21.6° C.
12.2° C.	21.7° C.
12.2° C.	21.7° C.
12.1° C.	21.6° C
Average. 12.16° C.	21.60° C.

Rise in temperature of water ..... 9.44° C.
Weight of water heated ..... 3.164 Kg.
Temp. of waste gases ..... 66° F.
Room temp ..... 72° F.
Gas burned, uncorrected ..... 0.200 cu. ft.
Gas burned, corrected ..... $0.2 \times 0.965 \times 0.996 = 0.192$ cu. ft.
Heating value ..... $\frac{3.164 \times 9.44 \times 3.968}{0.192} = 617$ B.t.u.

Had the English system of weights and measures been used throughout, the calculation would have been simplified by the elimination of the factor 3.968 and would have become

Gas burned, corrected $= 0.192$ cu. ft.
Water heated $= 6.97$ lb.
Rise in temp. of water $= 17.0°$ F.
Heating value $= \frac{6.97 \times 17.0}{0.192} = 617$ B.t.u.

12. Gross and Net Heat Values.—The method of calculation of the preceding section gives the amount of heat which would be imparted to the calorimeter if the products of combustion were cooled in the instrument to the temperature of the gas and air which were burned and escaped from the instrument with the same amount of moisture which they brought to it. It gives the maximum utilizable heat and so is often called the gross heat value. In the absence of any specification to the contrary the term heat value is to be understood to mean gross heat value.

In most industrial operations the combustion gases are not cooled to room temperature before escaping from the apparatus

and therefore some of the heat of the gas is wasted. This is due to a lack of efficiency of the apparatus and varies with individual conditions. There are so many industrial operations, however, where the water formed in combustion escapes as steam and the latent heat of steam formation is so large when compared with the amount of heat required to raise the temperature of fixed gases or of water or steam through moderate temperature intervals that the value of the latent heat is frequently deducted from the gross heating value. The resulting lower value is called the net heating value. The heat absorbed when one gram of water at 100° C. changes to steam at the same temperature is 0.536 Calories. The heat absorbed in the change of liquid water at 10° C. to vapor at 10° C. is very closely 0.600 Calories. This latter figure is usually employed in calculating the net heating value which is obtained by multiplying the number of cubic centimeters of condensed water dripping from the calorimeter during the combustion of a cubic foot of gas by 0.6, and 3.968 to convert into British thermal units and then subtracting this value from the gross heat value in British thermal units per cubic foot. The method of calculating the net heating value in the test reported in the preceding section is as follows:

Meter reading at start..... 21.200
Meter reading at close..... 22.100
Gas burned..... 0.900 cu. ft. uncorrected
Gas burned corrected, $0.9 \times 0.965 \times 0.996 = 0.86$ cu. ft.
Condensed water collected, 21.8 c.c.
Condensed water formed per cu. ft. gas $\frac{21.8}{0.86} = 25.4$ c.c.
Latent heat of condensed water $25.4 \times 0.6 \times 3.968 = 60$ B.t.u.
Net heating value of gas $617 - 60 = 557$ B.t.u.

13. Accuracy of Method.—The accuracy of the Junkers Calorimeter was thoroughly investigated in 1905 by Immenkotter[1] and in 1908 and in subsequent years by the Committee on Calorimetry[2] of the American Gas Institute which made a comparative study of the Junkers Calorimeter as compared with other

[1] *Jour. für Gasbel.*, 48, 736.
[2] *Proc. Am. Gas Inst.*, 1908, 285; 1909, 148; 1912, 65.

continuous flow instruments. Both investigations agree as to the substantial accuracy of the Junkers calorimeter.

The sources of error are as follows:

1. Registration of gas volume.
2. Measurement of temperature.
3. Measurement of water heated.
4. Incomplete combustion.
5. Sensible heat and uncondensed water vapor escaping in combustion gases.
6. Heat lost by radiation.

Errors in Registration of Gas Volume.—If the meter is in good condition and is calibrated after the water level has been adjusted the error of the meter need not exceed one-tenth of 1 per cent. If these precautions are neglected the error may be large. The error of observation will be about one small division of the large scale corresponding to 1 part in 200 or 0.5 per cent. error in a test as ordinarily run.

Errors in Measurement of Temperature.—If the thermometers are accurately calibrated, the water supply of constant temperature and the consumption of gas and its heat value constant during a test, there should be practically no instrumental error. If the constancy of any of these conditions is upset there will be errors due partly to lag in the thermometers which do not instantly respond to the changed condition. An error which is negligible except in the most accurate work is that caused by the different temperature of the bulb and the stem of the thermometer. There will be no correction for the emergent stem of the inlet thermometer if the inlet water is at room temperature. If the room temperature is 70° F., and the temperature of the outlet water is 90° F., an addition of from 0.07 to 0.10° F., should be made to the observed reading of the outlet thermometer, the exact amount depending on the depth to which the stem of the thermometer is immersed in the water. Detailed tables giving these corrections may be found in the Proceedings of the American Gas Institute for 1912 and also in a pamphlet published by the American Gas Institute entitled Directions for Erecting and Operating Gas Calorimeters. A more important error due to changed conditions during a test results from the large volume of water always contained in the

calorimeter. The Junkers calorimeter contains approximately 1500 grm. of water so that if a 2000 c.c. cylinder is being used to catch the water, it will have become three-quarters full before any of the water whose temperature at the inlet has been taken reaches the thermometer at the outlet. It will be evident that the larger the volume of water in the calorimeter the greater is the possible error from this source. The error in making a single reading of the thermometers should be less than a tenth of a degree and the mean error of a series of seven observations should not be over 0.05°. On a rise of ten degrees this corresponds to 0.5 per cent. This average of seven readings will not give the correct mean temperature of the water unless the individual readings differ from each other only by a few tenths of a degree.

Errors in Determination of Mass of Water Heated.—If the water is measured in a two liter cylinder the error of the observation will hardly be less than 10 c.c. or 0.5 per cent. and may be twice as great. The error in weighing the water should be less than 0.1 per cent. but an error of a second in terminating the experiment means 25 c.c. of water. This is a greater time error than necessary but the probable error in this process will be 0.5 per cent.

Error Due to Incomplete Combustion.—When the calorimeter is properly adjusted, this error should vanish.

Errors Due to Sensible Heat and Uncondensed Water Vapor Escaping in Combustion Gases.—As the gases pass down through the calorimeter they meet water of progressively lower temperature until just before leaving the calorimeter they are surrounded by water of the temperature recorded by the inlet thermometer. They should therefore leave the instrument at a temperature within a few degrees of that of the inflowing water. With a theoretical air supply the error from this loss of sensible heat in the dry gas is less than 0.3 B.t.u. per degree of temperature difference per cubic foot of gas burned. According to the report made to the American Gas Institute,[1] the actual errors observed as due to this source were only 0.5 B.t.u. per degree per cubic foot even when the temperature of the inlet water was far from that of the room. The actual figures recalculated slightly are given below.

[1] *Proc. Am. Gas Inst.*, 1909, 168.

Temp. inlet water	Temp. exhaust gases	Difference between temp. exhaust gas and inlet water	Error in heat value due to sensible heat of dry gases of combustion, B.t.u.	Error per degree difference
Deg. F.				
39	45.6	+6.6	+3.7	0.56
49	54.2	+5.2	+2.7	0.52
59.6	63.2	+3.6	+1.8	0.50
70.4	72.4	+2.0	+1.0	0.50
80.5	81.5	+1.2	+0.3	0.23
89.3	88.6	−0.7	−0.5	0.70

The error due to water vapor in the exhaust gases may be more serious. The exhaust gases always leave the calorimeter saturated with water. The gas burned having passed through a wet meter is also practically saturated with water. The air for combustion, whose theoretical volume for illuminating gas is roughly six times the volume of the gas, and whose actual volume may be twice that, is drawn from the room and may vary widely in humidity. The maximum error which can thus be introduced may be indicated by the following calculation. It is assumed that one volume of gas is burned with six volumes of air and that the volume after combustion contracts to six volumes. The water formed in combustion will remain in the vapor form so far as the gases can hold it and the remainder will condense in the calorimeter. The one volume of gas burned entered the calorimeter saturated with water so that only additional water to saturate 5 cu. ft. need come from combustion. The weight of water vapor per cubic foot of gas will vary with the temperature as shown in the following table.

Temp.	Wt. vapor in mixed cu. ft. gas and vapor
32° F	0.000304 lb.
42° F	0.000440 lb.
52° F	0.000627 lb.
62° F	0.000881 lb.
72° F	0.001221 lb.
82° F	0.001667 lb.
92° F	0.002250 lb.

The following examples will serve as an illustration of the use of these figures.

(1) Assume that the air enters at 62° and 50 per cent. saturated with water vapor, the gas enters at 62° saturated with moisture and the exhaust gases escape at 82°.

Moisture brought in 6 cu. ft. air at	0.00044 = 0.00264 lb.	
Moisture brought in 1 cu. ft. gas at	0.00088 = 0.00088 lb.	
		0.00352
Moisture carried out by 6 cu. ft. gas at	0.00166	0.01000
Excess of moisture supplied from water of combustion		0.00648 lb.

Latent heat = 1070 B.t.u. per lb.

Heat lost = $0.00648 \times 1070 = 6.9$ B.t.u.

This is an unusually large error since there is no need of letting the exhaust gases escape at such a high temperature. If they had escaped at 72° the error from this source would have been only 4.1 B.t.u. If they had escaped at 62° the error would have been only 1.9 B.t.u. If they had escaped at 52° or 10° below room temperature the error would have been almost zero.

This error is present in almost all operations but when care is taken to have the temperature of the exhaust gases a few degrees below that of the room the error should not be over 3 B.t.u. It will usually make the result too low but in cases where the room is warm and the air nearly saturated with water it may be in the other direction.

The most accurate results are obtained by keeping the temperature of the gas and the exhaust at room temperature and correcting for the humidity of the air according to the following table compiled by the Bureau of Standards.[1] Under these conditions the error will be about 1 B.t.u. Before using this table the humidity of the air must be determined as directed in the following Section. The corrections are expressed in B.t.u.'s and are to be added where the sign is + and subtracted where it is −.

[1] *Proc. Am. Gas. Inst.*, 7, 223 (1912).

CORRECTIONS TO OBSERVED HEAT TO GET TOTAL HEAT VALUE. AIR, GAS AND EXHAUST MUST BE AT THE SAME TEMPERATURE

If 7 volumes of air per volume of gas are used

Humidity per cent.	Room temperatures					
	65°	70°	75°	80°	85°	90°
10	+4.8	+5.7	+6.7	+7.9	+9.2	+10.5
20	+4.1	+4.9	+5.7	+6.8	+7.8	+ 9.0
30	+3.4	+4.1	+4.7	+5.6	+6.5	+ 7.4
40	+2.7	+3.2	+3.7	+4.5	+5.2	+ 5.9
50	+2.0	+2.4	+2.8	+3.4	+3.8	+ 4.3
60	+1.3	+1.6	+1.8	+2.2	+2.5	+ 2.8
70	+0.6	+0.8	+0.8	+1.0	+1.2	+ 1.2
80	−0.1	±0.0	−0.1	−0.1	−0.1	− 0.3
90	−0.8	−0.9	−1.1	−1.3	−1.5	− 1.9
100	−1.6	−1.8	−2.0	−2.4	−2.8	− 3.4

Loss of Heat by Radiation.—The calorimeter is protected against interchange of heat with the outside air by an insulating air chamber enclosed in a polished metal jacket. The efficiency of this protection is given in the report of the Committee on Calorimetry of the American Gas Institute for 1908 as 99.5 per cent. The metal jacket should be kept bright in order to maintain this efficiency.

Accuracy of the Process as a Whole.—None of the various preceding sources of error need amount to over 0.5 per cent. They will partially offset one another. When great care is taken the total error may not be over 1 per cent. Under ordinary conditions it is not safe to assume that the error will be less than 2 per cent.

14. Determination of Humidity of Air.—The following directions for the measurement of atmospheric moisture are given by the U. S. Weather Bureau.[1] The most reliable instrument for this purpose is the sling, or whirled psychrometer. In special cases rotary fans, or other means, may be employed to move the air rapidly over the thermometer bulbs. In any case satisfactory results cannot be obtained from observations in relatively stagnant air. A strong ventilation is absolutely necessary to accuracy.

[1] U. S. Dept. Agriculture, W. B. No. 235, Psychrometric Tables.

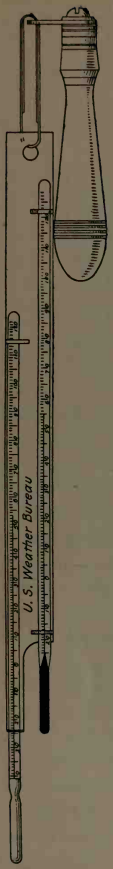

FIG. 25.—Sling psychrometer.

The sling psychrometer consists of a pair of thermometers, provided with a handle as shown in Fig. 25, which permits the thermometers to be whirled rapidly, the bulbs being thereby strongly affected by the temperature of and moisture in the air. The bulb of the lower of the two thermometers is covered with thin muslin, which is wet at the time an observation is made.

It is important that the muslin covering for the wet bulb be kept in good condition. The evaporation of the water from the muslin always leaves in its meshes a small quantity of solid material, which sooner or later somewhat stiffens the muslin so that it does not readily take up water. This will be the case if the muslin does not readily become wet after being dipped in water. On this account it is desirable to use as pure water as possible, and also to renew the muslin from time to time. New muslin should always be washed to remove sizing, etc., before being used. A small rectangular piece wide enough to go about one and one-third times around the bulb, and long enough to cover the bulb and that part of the stem below the metal back, is cut out, *thoroughly wetted* in clean water, and neatly fitted around the thermometer. It is tied first around the bulb at the top, using a moderately strong thread. A loop of thread to form a knot is next placed around the bottom of the bulb, just where it begins to round off. As this knot is drawn tighter and tighter the thread slips off the rounded end of the bulb and neatly stretches the muslin covering with it, at the same time securing the latter at the bottom.

To make an observation, the so-called wet bulb is thoroughly saturated with water by dipping it into a small cup or wide-mouthed bottle. The thermometers are then whirled rapidly for fifteen or twenty seconds; stopped and quickly read, the *wet bulb* first. This reading is kept in mind, the psychrometer imme-

diately whirled again and a second reading taken. This is repeated three or four times, or more, if necessary, until at least two successive readings of the wet bulb are found to agree very closely, thereby showing that it has reached its lowest temperature. A minute or more is generally required to secure the correct temperature. In whirling and stopping the psychrometer the arm is held with the forearm about horizontal, and the hand well in front. A peculiar swing starts the thermometers whirling, and afterward the motion is kept up by only a slight but very regular action of the wrist, in harmony with the whirling thermometers. The rate should be a natural one, so as to be easily and regularly maintained. If too fast, or irregular, the thermometers may be jerked about in a violent and dangerous manner. The stopping of the psychrometer, even at the very highest rates, can be perfectly accomplished in a single revolution, when one has learned the knack. This is only acquired by practice, and consists of a quick swing of the forearm by which the hand also describes a circular path, and, as it were, follows after the thermometers in a peculiar manner that wholly overcomes their circular motion without the slightest shock or jerk. The thermometers may, without very great danger, be allowed simply to stop themselves; the final motion in such a case will generally be quite jerky, but, unless the instrument is allowed to fall on the arm, or strikes some object, no injury should result.

The tables from which humidity may be calculated form Table IV of the Appendix and give the data for a barometric pressure of 29.0 inches of mercury. Their use is illustrated by the following example.

Air temperature $t = 75.0°$ F.
Wet bulb reading $t' = 66.0°$ F.
$t - t' = 9.0°$ F.

In table opposite 75° in column 9.0 is found 63.
Relative humidity = 63 per cent.

If the barometric pressure had not been 29 in. a slight error would have been introduced whose magnitude may be judged from the following examples of the same problem at different barometric pressures.

Barometric pressure 30	Relative humidity 63
Barometric pressure 27	Relative humidity 63
Barometric pressure 25	Relative humidity 64

The Weather Bureau report 235 referred to above gives fuller tables and may be obtained from the Bureau for 10 cents.

15. Non-continuous Water Heating Calorimeters.—In the third edition of his Gas Analysis, Hempel described a calorimeter where a volume of about a liter of gas was measured in a glass cylinder, passed through a small burner and burned in a stream of oxygen within a calorimeter containing a known mass of water. The rise in temperature of the water gave the data for the calculation of heat value, after the instrument had been calibrated by the combustion of hydrogen.

The *Graefe calorimeter* is a more recent commercial instrument of the same general type but somewhat larger. The instrument is rather crudely constructed and allows the exhaust gases to escape at an unduly high temperature so that it is necessary to calibrate it against some standard calorimeter. An inherent defect in calorimeters of this type comes from the increasing temperature of the exhaust gases as the test proceeds and the water of the calorimeter becomes warmer.

The *Parr*[1] *calorimeter* aims to compensate for this error and errors due to moisture in the exhaust gases by providing two duplicate calorimeters, one of which runs on pure hydrogen while the other is testing the unknown gas. The variation from the correct result shown by the hydrogen calorimeter is taken as the correction to be applied to the other result. The Committee on Calorimetry of the American Gas Institute in its 1912 report states that this calorimeter if properly operated gives correct results but that it is rather complicated in construction and requires more skill for its proper operation than the other types. The instrument gives gross heating values only.

The *Doherty calorimeter* is a compact instrument which measures the gas in an annular cylinder surrounding the combustion chamber and its water jacket. The gas is displaced by the warmed water which has flowed through this water jacket or heat absorption chamber, and thermometer readings are taken as the

[1] *J. Ind. and Eng. Chem.*, 2, 337 (1910).

water level passes fixed points on the gage glass. No meter is required and the water is neither weighed nor measured. The Committee on Calorimetry of the American Gas Institute in its 1912 report states that this calorimeter when operated properly gives the same efficiency as the Junkers calorimeter.

16. Automatic and Recording Gas Calorimeters.—The formula for the calculation of the heating value of a gas as given in § 11 of this chapter is $\text{H.V.} = \frac{m(t'-t)}{v}$. It is evident that if the ratio $\frac{m}{v}$ can be kept a constant and t can also be kept constant that the heating value can be readily determined from a single reading of t′ or can be continuously determined by a recording thermometer showing the temperatures of the outlet water. In the Junkers continuous calorimeter the ratio $\frac{m}{v}$ is kept constant by passing both gas and inlet water through meters whose drums are geared together by a chain forcing them to always rotate proportionately. There are various other types of automatic calorimeters. In every case they should be checked occasionally by a direct determination with a standard instrument.

17. Calculation of Heating Value from Chemical Composition.—If the heat value and the proportion of each constituent in a mixed gas were accurately known, it would be possible to calculate the heating value oft he mixture with entire accuracy. The following table gives the usual values in Calories per gram molecule and also the values recalculated by Earnshaw[1] to British thermal units at 60° F. and 30″ of mercury pressure.

Gas	Formula	Calories per gram molecule	B. t. u.'s per cu. ft. at 60° and 30″
Hydrogen	H_2	68,360	326.2
Carbon monoxide	CO	67,960	323.5
Methane	CH_4	211,930	1009.2
Ethane	C_2H_6	370,440	1764.4
Propane	C_3H_8	529,210	2521.0
Butane	C_4H_{10}	687,190	3274.0
Ethylene	C_2H_4	333,350	1588.0
Propylene	C_3H_6	492,740	2347.2
Butylene	C_4H_8	650,620	3099.2
Acetylene	C_2H_2	310,050	1476.7
Benzene	C_6H_6	799,350	3807.4

[1] *Jour Franklin. Inst.*, 146, 161 (1898).

If each constituent in the gas were known, the heating value calculated from this data would probably give accurate results. However, when it is noted that among the olefines, propylene has a heating value approximately 50 per cent. greater than ethylene, and butylene a heating value almost double that of ethylene it will be seen that there is dangerous latitude for arbitrary assumptions as to the constituents of the olefines. When the "illuminants" as reported include not only the olefines but benzene the error involved in an arbitrary assumption of the mean heat value becomes still greater. The varying members of the methane series also possess widely differing heating values. Earnshaw, in the reference cited gives an analytical method for determining the mean composition of the olefines and for differentiating between methane and ethane. The method is, however, difficult analytically, and the results when obtained are not entitled to the degree of confidence which pertains to those obtained directly in a calorimeter.

The probable error involved in this method of calculating the heating value of gas (unless Earnshaw's complex analysis is followed out) is about 5 per cent. In the case of carburetted water gas it is still higher. In the case of producer gas where the total percentage of hydrocarbon is low *and where all suspended tar particles have been removed* the results are more accurate.

1.— Rate of emission of energy
2. Quantity of energy
3.— Different rates in different dir

CHAPTER VIII

CANDLE POWER OF ILLUMINATING GAS

1. Introduction.—Photometry deals with the measurement of the intensity of light. The term light as used here includes only those rays which excite vision in the human eye, which thus necessarily becomes the final arbiter in photometric tests. The eye cannot estimate absolutely the amount of light which stimulates it. It can compare roughly the intensity of illumination from two sources and it can determine with more precision when the intensities from two sources are the same. In the sense in which it is here used, photometry consists in the comparison of two lights, one of which is a standard. The photometer is a device which assists the eye in determining when the two lights are of the same intensity. The intensity of light entering the photometer is changed by varying the distance between the photometer and the light, the intensity of light from a given source varying inversely as the square of the distance. When the adjustments have been made so that the intensity of light impinging on the photometer from the two sources is the same, as shown by the equal illumination of the two photometer faces, the ratio of the unknown light to the standard light becomes mathematically calculable from the relative distances of the lights from the point of equal illumination. The value of luminous intensity is in English-speaking countries and in France expressed in candle-power.

2. Method of Rating Candle-power.—The light emitted from a single incandescent particle would illuminate uniformly every point of an enveloping sphere and the intensity of illumination might be measured equally well at any point on the sphere. When the light to be measured comes from a surface of finite size as is always the case in practice, there is interference with the free path of the light waves from a single particle in one or more directions so that the illumination of the enveloping sphere is no longer

uniform. It is possible by the use of reflecting mirrors to determine the illumination at various points on the circumference of a polar circle and to plot from this data a curve showing the distribution of light at various angles. Methods of this sort are often resorted to in a study of illumination where it is desired to determine the value of a light source for a particular purpose. This method is, however, rarely followed where it is simply a question of testing the quality of the gas. The simpler custom of taking the horizontal candle-power given by a conventionalized burner under conventional conditions as indicating the value of the gas, has become well established.

3. The Bar Photometer.—The bar photometer consists of a graduated bar which carries at one end a standard light and at the other end the test light. Upon the bar slides a carriage with an apparatus for comparing the illumination from the two sources. The carriage is to be moved back and forth until the point is found where the illumination from the two lights is equal, and its position on the graduated bar recorded. If now the distance of the comparison box from the standard light be called "a" and that from the unknown light "b," then the illumination of the unknown as compared with the standard light is expressed by the proportion,

$$\frac{\text{unknown}}{\text{standard}} = \frac{b^2}{a^2}$$

There are many modifications of this type of photometer but all involve the four essentials: a standard light, the unknown light, a photometric screen and a means of measuring the distance of each light from the comparison box. It is customary to have the two lights fixed at opposite ends of the bar, in which case the sum of a+b in the preceding formula is a constant. Sometimes however the standard lamp is placed on a sliding carriage connected by a rigid link with the photometric screen so that the distance "a" of the formula becomes a constant. A modification of the bar photometer in use in England is the table photometer where the two lights and the comparison box are all rigidly fastened at the points of a triangle. Comparison is effected by varying the rate of combustion of the gas being tested until equality of illumination is reached. Its candle-power is then mathematic-

ally determined. This method of determining candle-power is not in use in Germany or America.

The various essential parts of a bar photometer will be considered separately and the details of its operation will then be described.

4. Standard Light.—The early photometrists used as their standards candles of varying size. In 1860, the English parliament adopted as standard the sperm candle 7/8 in. in diameter and burning at the rate of 120 grains per hour. In 1884, Hefner v. Alteneck brought out the amylacetate lamp which has become the most generally used standard for testing the candle-power of gas. The Harcourt 10 candle pentane lamp was proposed in 1898 and has been adopted as the official source of light by the Gas Referees of London. It has many advantages. All of these flame standards vary materially in candle-power with change in atmospheric conditions and are, for scientific work, to be corrected to standard conditions of temperature, pressure, humidity and percentage of carbon dioxide in the air. In ordinary work when used in measuring candle-power of gas flames they are however not thus corrected but the assumption is made that the standard light and the gas light are equally affected by atmospheric conditions.

The only satisfactory standard not affected by atmospheric conditions is the incandescent electric lamp. Incandescent lamps properly aged may be bought with the certificate of the Bureau of Standards and furnish the most reliable photometric standards when used under proper conditions. These conditions, however, require that the lamp shall be supplied with current at perfectly definite voltage from a large storage battery equipped with suitable rheostats and electrical measuring instruments so that the installation is an expensive one, and is used only in research laboratories. When the incandescent electric standard is used in the photometry of gas flames correction must be made for the effect of atmospheric conditions on the flame. This correction is not infrequently as much as ten percent, and has been accurately determined for only a few of the standard lights.

5. Photometric Units.—The international candle is the common unit of intensity in England, France and America, having been officially adopted by agreement of the government standardising

laboratories of the three countries in 1909. Prior to that date the official unit in this country had nominally been the British Parliamentary candle but there had not been definite agreement as to its value. In Germany the photometric unit is the Hefner which equals 0.90 International Candles. Conversely 1 International Candle equals 1.11 Hefners. The history of the adoption of the International Candle may be found in the reports of the Bureau of Standards and in the Proceedings of the American Gas Institute.[1]

Although there is thus an international unit of light, the international candle, it does not follow that this unit is best obtained by burning any actual candle. In fact various other standard lights are preferable.

6. Standard Candles.—In 1860 the Gas Referees of the City of London adopted as their unit the light emitted by a sperm candle of 1/6 lb. weight when burned at the rate of 120 grains per hour. From time to time they issued specifications for the manufacture of candles to fulfill this requirement but were never successful in ensuring uniform quality and in 1897 entirely discontinued the use of candles. The Dutch Photometric Commission reported in 1894, after an exhaustive study, that the average light from a good English Parliamentary candle might exceed or fall below that of the average candle by nine per cent. The use of candles as standards is deservedly decreasing.

When candles are to be used they are burned on a candle balance placed on the photometer bench. A simple form of balance is illustrated in Fig. 26. A long candle is cut in two and both halves used simultaneously. They are to be allowed to burn until the cups have formed normally and the wicks have bent over till the tips are glowing in the outer flame. The candles are then to be turned so that the glowing end of one wick points towards the photometer and that of the other points in a direction at right angles to that of the first. They should project 1 to 1 1/2 in. above the holder and should burn clearly and without guttering. When all is in readiness for a test, the counterpoises are adjusted so that the candles are slightly too heavy for a perfect balance. As they burn away the pointer on the scale falls and as it passes the zero mark the stop watch is

[1] *Proc. Am. Gas Inst.* 2, 454, 528 (1907); 3, 403 (1908); 4, 78 (1909).

started. A 20-grain weight is then placed on the pan below the candles and photometric readings are made each half-minute. At the expiration of four and a half minutes the observer returns to the candle balance and stops the watch when the pointer again is at the zero mark, indicating that the 20 grains of sperm have been burned. If the candles are burning at exactly the proper rate the watch should show that exactly five minutes have elapsed. If the variation in the amount of sperm burned per hour is not over 5 per cent. from the standard amount it is permissible to make a mathematical correction, the assumption

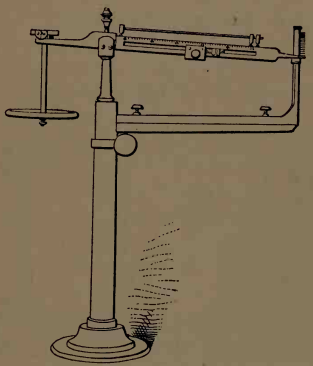

FIG. 26—Candle balance.

being that the light evolved is in direct proportion to the weight of candles burned. If the observed weight of sperm burned by the two candles is 250 grains per hour instead of 240 the value of the light is said to be $2 \times \frac{250}{240} = 2.08$ candles. If the deviation is greater than 5 per cent. the test must be rejected and a different candle used. Improper ventilation and too high a temperature in the photometer room will affect the burning of the candles. This subject is discussed in § 18.

7. The Hefner Lamp.—The dimensions of the Hefner lamp have been rigidly specified by the German Reichsanstalt[1] which

[1] *Jour. für Gasbel.*, 36, 341 (1893).

will certify a lamp to be correct if it is mechanically properly made and gives a light which does not differ more than 2 per cent. from the official lamp of the Reichsanstalt. The construction of the lamp is shown in Fig. 27. It consists of a brass bowl into which a head screws carrying the German silver wick tube and the mechanism for controlling the height of the flame. The flame height is determined by a gage which clamps to the head-piece. The older form of gage shown at A consists of two sights, one on each side of the flame. The newer Krüss optical gage shown at C consists of a ground glass screen and a magnify-

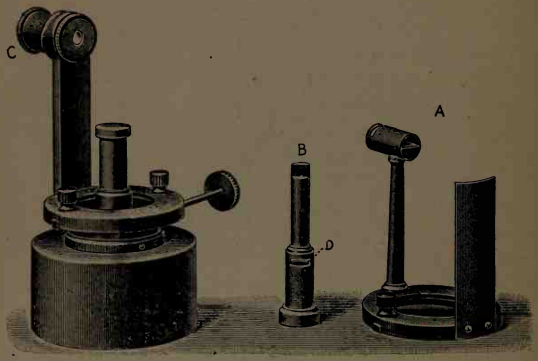

FIG. 27.—Hefner lamp.

ing lens which allows more delicate adjustment of the flame tip to the horizontal line across the gage. Each lamp is provided with a control gage shown at B which fits over the wick tube and sits squarely on the head-piece. With the control gage in this position and the lamp level an observer looking toward the light should see through the openings D a very fine ray of light less than 0.1 mm. wide between the top of the wick tube and the control gage, and looking through the optical gage should see the cross-hair in exact coincidence with the broad top of the control gage. The wick tube is screwed into the head-piece and if it becomes necessary to change its height the control gage,

inverted, is to be pushed down the wick tube and used as a handle. The exact material of which the wick is made is not of importance but it must fill the tube snugly but not tightly. It is best to use only that furnished by the manufacturers. The amyl acetate must be of good quality and certified to be fit for photometrical purposes. The German Gas Association sells properly certified amyl acetate in one liter bottles.

In using the Hefner lamp the bowl is to be filled about two-thirds full of amyl acetate and after the wick has been moistened by capillary action it is to be screwed somewhat above the wick tube and cut squarely off. The lamp is then to be lighted and allowed to burn at least ten minutes with occasional regulation of the flame height before a test is commenced. The temperature of the photometer room should be between 60° and 70° F. The lamp is to sit on a horizontal support in a room free from drafts and adequately ventilated.

The flame height of the Hefner lamp is to be carefully adjusted since a deviation of 1 mm. from the correct flame height of 40, introduces an error of about 3 per cent. It is the luminous tip of the flame which is to be 40 mm. high. With the Krüss optical gage the frosted glass cuts out the almost colorless outer flame so that there is no possibility of confusion. With the older Hefner gage the luminous tip should appear tangent to the lower edge of the sighting plane.

If the lamp is used only infrequently it should be emptied after use and both lamp and wick should be washed with alcohol. It is wise to throw away the old amyl acetate and clean the lamp in this manner at intervals even when it is in frequent use since the amyl acetate decomposes somewhat on standing.

The Hefner lamp gives a light of 0.9 international candles when burned in pure air under 760 mm. barometric pressure and containing 8.8 liters of water vapor per cubic meter. Although atmospheric conditions must be controlled and correction made in exact scientific work corrections are usually omitted in taking candle-power of gas on the assumption that atmospheric conditions affect the Hefner lamp and the gas burner to a similar degree. The errors involved in this assumption are discussed briefly in § 18. The Hefner lamp is a very widely used standard. It is portable, cheap, and accurate. Its disadvantage is its low candle-

power, and the tendency of the flame to flicker, especially at summer temperature.

8. The Pentane Lamp.—The 10 candle pentane lamp or Harcourt lamp was adopted as standard by the London Gas Referees in 1898.[1]

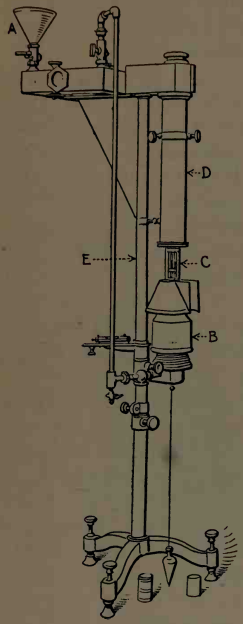

FIG. 28.—10 candle power pentane lamp.

Fig. 28 shows this lamp with some improvements in details recommended by the Bureau of Standards and added by the American manufacturers. In this lamp air entering at A passes over pentane and becomes saturated with pentane vapor. The air-gas so formed descends by gravity to an Argand burner B enclosed in a metal hood. The flame is drawn into a definite form and the top of it is hidden from view by a long brass chimney C. The chimney is surrounded by a larger brass tube D in which air, warmed by the chimney, rises and descends through the tube E, which is also the main standard of the lamp, to the center of the Argand burner where it aids in the combustion of the gas. The lamp may be obtained with the certificate of the Bureau of Standards.

Before using the lamp the saturator is to be filled abou ttwo-thirds full of pentane and both cocks on the saturator are to be closed. As pentane is very volatile and mixtures of its vapor and air within certain proportions are explosive care must be taken that no flames are burning in the room while the lamp is being filled. The inner chimney above the burner must be centered by the adjusting screws, turned so that the mica window is away from the photometer box and set at the proper height by placing on the burner the 47 mm. block which accompanies the

[1] *Jour. of Gas Lighting*, 71, 1253 (1898).

lamp, and lowering the chimney till it rests lightly on the block. To prepare the lamp for lighting, open the outlet cock on the saturator and the drip cock. This will fill the feed pipe with pentane vapor and air. Open the inlet cock on the saturator, close the drip cock, open the regulating cock at the burner and light the gas at once. It requires about fifteen minutes for the flame to become constant and during this period the top of the flame should be kept approximately on the cross bar of the mica window. The lamp should be set for maximum luminosity which condition is attained when the flame is just high enough so that the non-luminous upper portion is cut off from the photometric screen by the chimney. In case of doubt the proper setting may be determined by lighting the gas flame at the other end of the bench and determining with the photometer the setting of the lamp which gives maximum illumination.

In leaving the lamp after a test both the inlet and the outlet cocks of the saturator should be closed. After about a gallon of pentane has been burned the liquid remaining in the saturator should be emptied out and thrown away.

9. Secondary Standards of Light.—The Hefner lamp, the 10 Candle Pentane lamp and, to a lesser degree, standard candles are primary standards since they are readily reproducible. There are various secondary standards which are convenient to use when frequent candle-power determinations are to be made but which must be standardized at intervals by direct comparison with a primary standard. Most of these standards are based on the fact that the brightest portion of a lamp flame is of almost constant luminosity.

The Edgerton Standard burner consists of a Sugg "D" burner provided with a glass chimney 1 3/4 in. in diameter and 7 in. high. Outside of this glass chimney is a brass sleeve with a horizontal slot 13/32 of an inch high through which the light passes to the photometer. This is nominally a five candle-power standard but will actually vary from four to seven candles. After the value with a given gas has been fixed it will not vary much if the candle-power of the gas feeding it does not vary over two candles. The chimney must be cleaned frequently and the lamp restandardized each time a new chimney is put into service.

The Elliot lamp is a student lamp of special design with a

flat wick and a rather large chimney and a screen which cuts off all but the desired portion of the flame. The lamp uses kerosene as its fuel and is nominally a ten candle-power lamp. Its illuminating value with a single lot of good kerosene is of very satisfactory constancy.

10. Standard Gas Burners.—At the time when gas testing commenced to be standardized the Argand burner was the form in common use. This type was therefore naturally adopted as the standard. It was also recognized that it was only right to

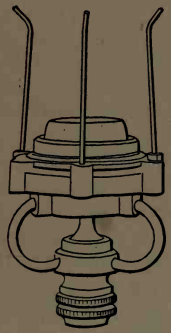

Fig. 29.—D Argand burner.

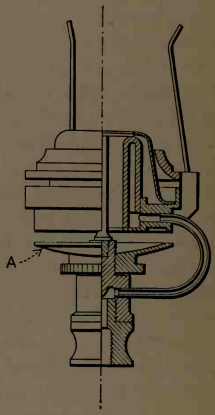

Fig. 30.—Metropolitan No. 2 Argand burner.

test the gas in a burner which was adapted to it and therefore various standards came into vogue in England, such as the Sugg D Argand illustrated in Fig. 29, which is intended for gases of less than 16 candle-power. The Sugg F burner is intended for gases of 16–20 candle-power.

In 1905, in connection with a readjustment of the price and candle-power of the gas supplied in London the Gas Referees were directed by Parliament to use a burner adapted to obtain from the gas the greatest amount of light when burned at the rate of five cubic feet per hour. In accordance with these instruc-

tions the Gas Referees adopted the Metropolitan No. 2 Burner shown in Fig. 30. This burner differs from the older types mainly in having an adjustable air supply to the center of the burner. The burner is designed for all qualities of gas up to 20 candle-power. When lighting the burner the air regulating disc A is to be screwed down so that the full supply of air passes to the burner, and the burner is to be adjusted to approximately the five cubic foot rate. After allowing it to burn for fifteen minutes to become thoroughly warm the gas is to be adjusted carefully to the rate of 5 cu. ft. an hour, after which the air regulator is to be screwed upwards until the flame rises in the chimney as high as possible without smoking. The Metropolitan No. 2 Argand gives results materially higher than the ordinary Argand on gases of low candle-power.

Bray's No. 7 Slit Union burner is frequently used with carburetted water gas of more than 20 candle-power. The rate of gas consumption is as usual adjusted to 5 cu. ft. an hour.

11. The Bunsen and Leeson Photometric Screens.—The Bunsen photometric disc dates from 1841 and in its simplest form consists merely of a sheet of paper with a grease spot in the center. This is mounted so that it may be moved back and forth between the two lights. When looking toward the stronger light the translucent grease spot appears bright. As the carriage is slowly moved away from the stronger light the constrast between the spot and the surrounding paper diminishes and almost disappears when equality of illumination is reached. If the carriage is moved still further in the same direction the grease spot stands out dark against the white background. The paper screen is usually mounted in a box as shown in Fig. 34 where by an arrangement of mirrors the observer standing in front of the instrument may see both sides of the screen at once. This form of apparatus is still frequently used.

The Leeson star disc is a modification of the Bunsen screen. It consists of a piece of opaque paper from whose center is cut a star and which is pressed between two sheets of translcuent paper. It is a decided improvement on the Bunsen screen.

12. The Lummer-Brodhun Photometric Screen.—This is a very accurate form of photometer which is shown diagrammatically in Fig. 31 and in perspective in Fig. 32. It consists

of a series of reflecting surfaces and prisms which direct light rays from the two sources into a telescope tube. Light entering from the two opposite sources R and L is diffusely reflected by the

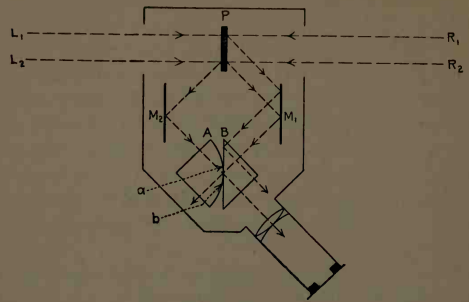

FIG. 31.—Diagram of Lummer-Brodhun photometric screen.

opaque plaster of paris disc P onto the mirrors M_1 and M_2 and by them to the prisms AB. The prism A has most of its hypothe-

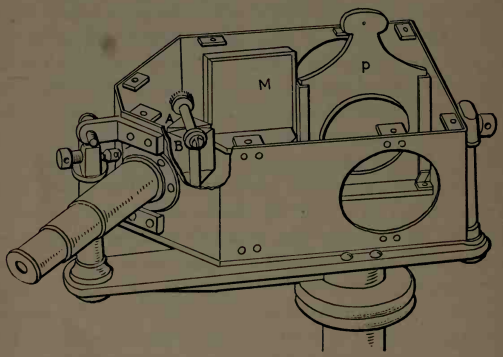

FIG. 32.—Lummer-Brodhun photometric screen.

nusal face ground away, only a small circular plane being left in the center. The two prisms are clamped closely together and become optically homogeneous over this small circular area shown

at ab. Of the light coming from L only that reaches the telescope which passes through this circular spot, the path of the rays being shown from L_2. Of the light from R, that which strikes the spot ab passes on undeflected and is absorbed by the black walls of the box. The path of these rays is shown from R_2. The other rays suffer total reflection into the telescope as shown in the rays from R_1. The image in the telescope appears, therefore, as a circular spot illuminated from L in a circular field illuminated from R. In this equality photometer when the illumination from the two sources is identical the spot and the field are not to be distinguished from one another.

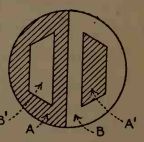

FIG. 33.—Field of Lummer-Brodhun contrast photometric screen.

In the Lummer-Brodhun contrast photometer advantage is taken of the physiological fact that the eye is able to perceive a smaller degree of difference in contrast than difference in brightness. By suitably cutting the prisms the image in the telescope is divided into four portions as shown in Fig. 33. In this figure the shaded trapezoidal space A′ is illuminated from the same source as the shaded semi-circular area A. Similarly B and B′ are illuminated from the same source. However, although the areas A and A′ are illuminated from the same source, they are not equally illuminated, for through the interposition of a plate of glass before A′ it receives about four per cent. less light than A. B′ is in the same way and to the same degree less brilliantly illuminated than B.

If, now, the light from the two sources is exactly the same both in intensity and color the semi-circular fields A and B will be identically illuminated and will not be distinguishable from one another. The trapezoidal figures A′ and B′ will also be identically illuminated and will stand out with the same relief from their respective backgrounds. This can only happen when A and B are equally illuminated. It affords a more sensitive ocular test of the equality of A and B than can be obtained by comparing them directly. The lights at the two ends of the bench are never of absolutely the same, and are sometimes of a widely differing, color. When a Welsbach light is tested against the Hefner lamp the field illuminated from the mantle burner is a clear blue color while the other is a yellow. The eye cannot determine with much

accuracy when the yellow field and the blue one are illuminated to the same extent, but it can determine with greater accuracy when the yellow trapezoid A′ stands out from its blue background with the same distinctness that the blue trapezoid B′ stands out from its yellow background. The eye judges slight contrasts more accurately than large ones and therefore it is most sensitive when the photometer is almost at the neutral point. It is well to make an approximate setting for equality of A and B and then focus the attention on the contrast between the trapezoids and their respective backgrounds and complete the adjustment.

13. The Flicker Photometer.—In the various forms of flicker photometer the light from each source is presented alternately and rapidly to the eye by means of revolving discs or prisms in the photometer box. When the intensity of light from the two sources is the same the flicker vanishes. No difficulty is experienced with lights of varying colors, but the photometer is fatiguing to the eye and its proper adjustment requires considerable skill.

14. The Gas Meter.—The meters used in photometric work are of the same general type of wet meter as those described in § 3 of Chapter VII for calorimetric work. They must be calibrated with the same care and used with the same precautions. It is more convenient, however, to use a smaller meter which passes only 1/12 cu. ft. per revolution. When the gas is being burned at the rate of 5 cu. ft. an hour this meter will make exactly one revolution a minute. The dial of the meter is graduated into five parts with finer subdivisions. An observation of one minute will therefore give directly the uncorrected gas consumption in cubic feet per hour. Great care must be taken to see that the water of the meter is saturated with gas of the sort that is to be tested, for the "illuminants" of the gas are relatively soluble in water and a slight change in their percentage makes an appreciable difference in the candle-power of the gas.

15. The Photometer Bench and Its Equipment.—The preceding sections have discussed the various types of standard lights, burners and photometers which may be used. It is evident that wide latitude may be exercised in the choice of units and the method of assembling them to form a photometer bench.

The details regarding the length of bar, type of standard light,

form of test burner, kind of comparison box, and the directions for testing are in some cases controlled by legal enactment and are in some cases matters of arbitrary choice. It is possible, however, to trace two distinct lines of influence, the English and the German. Of these the English is the older and the German the more scientific. Modern methods of testing show more and more the grafting of German methods onto the English stock. It is under all circumstances necessary that the meter, standard light, and gas burner be thoroughly reliable. The photometric screen

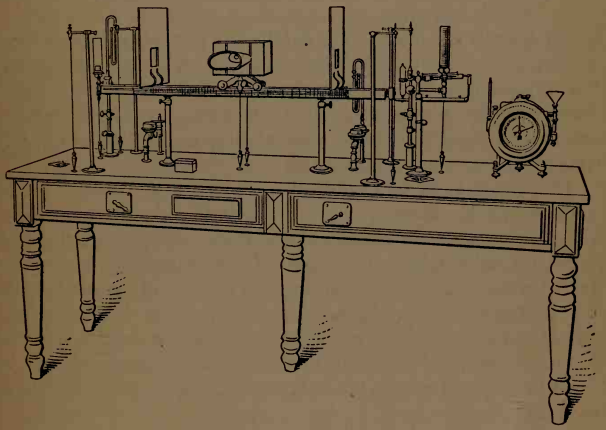

FIG. 34.—Photometer bench.

may be of cheaper type and the bench itself may be of simple wooden construction with the scale made of yard sticks joined together. The bar most commonly used in America is 60 in. long. This is sufficiently accurate where ordinary gas flames are being tested. For lamps of high candle-power longer bars are desirable.

A photometer bench frequently used is shown in Fig. 34. At the right hand end is shown the meter and next to it the candle balances in position, with the Edgerton standard burner on a swinging arm so that it may be used instead of the candles. At

the left hand end is the Argand burner for the gas and between the two the bar itself with its screens and photometer. The piping for the gas is entirely below the table top but the pressure regulators and gages are shown above the table at the back.

Precision photometers usually follow the German, or Reichsanstalt, pattern in which the bar is built up of a rigid steel track on which the carriage of the photometric screen travels. The standard light and the test light are usually also mounted on a travelling carriage with provision for clamping them rigidly at any desired point of the bench. The length of the bench may thus be varied at will.

16. Details of a Test.—The details of a test will of course vary with the equipment of the photometer bench and especially with the type of standard light employed. Directions for the use of these lights have been given in preceding sections. In the following paragraphs will be found general directions which are applicable to most forms of apparatus.

The meter is to be examined to see that the water-level is correct and if necessary more water is to be added. In case the test is unusually important the meter should be calibrated against a tank of known volume. The tightness of connections between the meter and the burner is to be assured by turning the gas into the meter while keeping the stopcock on the burner closed. The meter hand should not show any perceptible motion in one minute. If there is a small leak allowance may be made for it in the calculations, but it is vastly better to have the whole apparatus tight.

A clean chimney is to be placed on the Argand burner and the burner lighted. The pressure gage between the diaphragm governor and the burner should indicate about 1 in. of water pressure depending on the exact type of burner used. The consumption of gas is to be set so that the meter hand makes a revolution in approximately a minute and the light is then allowed to burn for at least fifteen minutes. If the meter has had much fresh water added to it, or if it was last used for a gas of a different quality than the one soon to be tested, or if the gas is being drawn from long lengths of pipes where the gas lies dead, a longer time than fifteen minutes must be allowed to elapse before commencing the test which must not be started until it is certain that the gas

burning is of representative quality and that it has not been changed by contact with the water of the meter.

The final adjustment of the gas is made after taking into consideration the meter temperature and the barometric pressure. The desired rate of consumption being 5 cu. ft. measured under standard conditions, the correct apparent rate may be mentally calculated by adding to the 5 ft. 0.01 cu. ft. for each degree Fahrenheit shown by the meter thermometer above 60, and adding 0.03 ft. for each 0.1 in. of mercury pressure below 30. For example, if the meter temperature is 80° F., and the barometric reading is 29.5 the uncorrected consumption of gas per hour should be $5.0+.20+.15=5.35$. The gas is to be set to this desired flow with an error of less than 1/10 cu. ft. The stop-watch is started as the hand crosses the zero and stopped after one complete revolution. It should read between 59 and 61 seconds. After the gas has been satisfactorily adjusted and the standard lamp given a final adjustment the test may be commenced.

The observer starts the stopwatch as the large hand of the meter passes the zero and steps quietly to the photometer avoiding sudden movements which would create drafts, and makes and records the first observation. Four more readings are made at intervals of about twenty seconds and then the photometric screen is reversed and five similar readings taken. If the lights flicker during an adjustment the observer must wait until the drafts have subsided before completing the observation. The series of ten observations usually requires about five minutes. At their conclusion the operator steps back to the meter and stops the watch as the large hand of the meter again passes the zero.

If a stopwatch is not available it is better to make the test during an even number of minutes rather than during the consumption of an even number of cubic feet of gas. If the observer holds the watch close to the meter and keeps his eyes on the watch till the second hand reaches the zero and then reads the position of the large meter hand, and follows the same precedure at the close of the test, the error will be well within the other necessary errors of the process. In case a stopwatch is available, it is more accurate to start the watch as the meter hand comes to its zero and to conclude the observation when the meter hand passes its zero, after the photometric observations have been completed.

17. Illustration of Calculation.—The calculation which follows is for a test made on a 2500 mm. bench with a Hefner light as the standard.

Date, Feb. 26.
Source of Gas. Proportional Tank. Test 42. Experimental Gas Plant.
Gas burned in London Argand.
Standard Light—Hefner.

	Time	Meter Reading
Commencement of Test	10 : 16 : 00 A. M.	47.8
End of test	10 : 21 : 00	50+24.6=74.6
Duration	5 : 00	

Cubic feet gas uncorrected..... 26.8
Cubic feet gas per hour uncorrected..... 5.36
Meter Temperature 80° F. Error in meter less than 0.1 per cent.
Barometer 29.5 inches. Correction factor..... 0.973
Cubic feet gas per hour uncorrected 5.36. Corrected..... 4.96
Bar Readings 454, 456, 455, 462, 460
460, 458, 460, 463, 464 Average 462.

Calculation $\left[\frac{(2500-462)^2}{(462)^2}=\frac{X}{.9}\right]\times\frac{5.00}{4.96}=17.6$ candle-power.

18. The Photometer Room.—The photometer bench must be placed in a room of reasonably constant temperature which is free from drafts and yet well ventilated. A room ventilated so that the carbon dioxide does not rise above ten parts in 10,000 during a test is as much as can be expected in ordinary work. The carbon dioxide may rise to twenty parts without the air being more polluted than in an ordinary crowded street car in winter. The water vapor normally present in the air and that given off by the flames and the respiration of persons in the photometer room exerts an even greater influence on flames than the carbon dioxide but since its accurate determination is difficult, the carbon dioxide is usually taken as the measure of contamination of the air.

The committee on Photometry of the American Gas Institute[1] have published some curves showing the variation of certain flames with increased carbon dioxide when compared with an incandescent electric lamp. The humidity of the air varied so

[1] *Proc. Am. Gas. Inst.*, 11, 480 (1907).

much from day to day that a comparison of one day's work with another could not be made and the following figures from their curves must be taken as merely illustrative of the large errors that may arise.

COMPARISON OF PENTANE LAMP WITH GAS FLAME

Parts CO_2 in 10,000	10.0	20.0
Per cent. loss of candle-power gas flame	4.0	20.0
Per cent. loss of candle-power pentane	7.5	31.0

COMPARISON OF PENTANE LAMP WITH CANDLES

Parts CO_2 in 10,000	10.0	20.0
Per cent. loss of candle power, candles	19.0	27.0
Per cent. loss of candle power pentane	13.0	16.5

It is therefore evident that the usual assumption that the standard light and the test light are equally affected by atmospheric conditions, is erroneous and that care should be taken to have the test made under as favorable atmospheric conditions as possible.

19. Jet Photometers.—There are two main types of jet photometers. In one type, gas passes through a pressure regulator and issues at constant pressure through a small round orifice where it burns in a jet whose height as read on the glass chimney is assumed to give candle power directly. In the other type of jet photometer the gas flame is kept at a constant height and the pressure required to force the gas through the burner opening is measured as an indication of candle powers. No type of jet photometer can be relied on to do more than give approximate determinations. They should be calibrated frequently against a bar photometer.

20. Accuracy of Photometric Work.—When it is recollected that the Reichsanstalt certifies a Hefner lamp as correct if it is within 2 per cent. of their standard, and that the absolute value of the pentane lamp may vary as much as 25 per cent.[1] in the course of a year on account of changing atmospheric conditions and further that the human eye is a very inaccurate scientific instrument, a greater accuracy than half a candle can hardly be

[1] J. B. Klumpp, *Proc. Am. Gas Light Assoc.*, 1905. Appendix.

expected with illuminating gas tested under ordinary conditions. Much larger errors may creep in unless care is taken.

The determination of candle power has largely lost its significance as a criterion for municipal gas supplies, since from 75 to 90 per cent. of the gas sold is used for heating, or in Welsbach burners, where the heat value is a much better criterion. The international Photometric Commission in 1911 passes the following resolution.[1]

"The International Photometric Commission is, after consideration of the present uses of illuminating gas, of the opinion that the illuminating value of gas flame has lost its significance and that the determination of the heating value should replace the determination of candle power as the most important criterion of its value."

[1] *Jour. für Gasbel.*, 1911, 1002.

CHAPTER IX

ESTIMATION OF SUSPENDED PARTICLES IN GAS

1. Introduction.—The estimation of particles held in suspension in gases is daily becoming of greater importance on account of legal restrictions on pollution of the air and on account of insistence on closer control of industrial operations by manufacturers. The problem is one of great difficulty and is usually susceptible of only approximate solution. Not only is it difficult to obtain the suspended solids present in a flue at a given point and time, but it is difficult to determine whether the solids thus determined were normal in amount or whether they were, for instance, low because of the deposition of an unusually large proportion prior to the point of sampling on account of slower velocity of gas in the main, or because of lower temperature or for some other reason.

2. The Distribution of Particles in the Cross-section of a Straight Main.—If the main is horizontal it is evident that there will tend to be a stratification of the particles, the large and heavy particles separating faster than the fine and light. This tendency to settle is, however, resisted by the whirling motion which gases traversing flues frequently possess and which is frequently caused by the inequalities in pressure produced by bends in the pipe. The velocity of gas in a straight main at ordinary working speeds is greatest at the center and least at the walls. The shape of the wave front varies with the speed of the gas, high velocities accentuating the difference. Solid particles are pushed gradually out of the zone of high velocity into one of lower velocity in the same way that a piece of wood in a river is gradually pushed to the still waters along the bank. This action takes place in a vertical as well as a horizontal main.

The solids contained in a gas at the point of greatest velocity will therefore be the least in amount, the smallest in size, and the lowest in specific gravity. The quantity of particles, their size and specific gravity will all increase in the regions where velocity

is least. In a normal round main this point of greatest velocity is the center where will be found the fewest and lightest solid particles. Their quantity and magnitude increase in successive rings to the circumference. If the velocity of the gas is decreased until the main is also acting as a settling chamber there will be little difference in the velocity throughout the cross-section and the region near the top of the main will contain the fewest solid particles.

This uneven distribution of suspended particles in a gas stream may take place very rapidly as was shown by the author[1] some years ago in an attempt to determine the amount of suspended tar in unpurified illuminating gas. A 14-in. main containing unpurified illuminating gas was tapped on its horizontal axis at a point a few feet beyond the exhauster and two sampling tubes inserted, one extending to the middle of the main and the other projecting through the wall only about an inch. Four tests were made and in each case the suspended tar caught in the sampling tube near the edge of the main was more than twice as great as that found in the tube projecting to the center.

3. Mean Velocity in the Cross-section of a Gas Main.—Threlfall[2] has shown that it is necessary to investigate the distribution of velocity for each individual case as it arises, but that in general the radius of the circle of mean velocity is about 0.775 of the radius of the pipe. In one case it was as high as 0.9 of the radius but in no case did it sink to 0.69 which is the figure quoted for water flowing through a long and smooth pipe. The radius of mean velocity did not change with varying speed of gas flowing through the pipe within the ranges of 600 ft. and 3600 ft. per minute, which marked the limit of the experiments. Threlfall's experiments were on pipes varying from 6 to 36 in. in diameter.

4. Influence of Bends in a Main.—If gas flowing through a straight main comes to a bend there will be a change in the relative velocities of the particles of the gas throughout the cross-section. The kinetic energy of a body is represented by the expression $1/2mv^2$ where m represents the mass of a body and v its velocity. It is evident therefore that the particles with the greatest mass and the greatest velocity will be projected beyond

[1] *Proc. Mich. Gas. Ass.*, 1906.

[2] *Proc. Inst. Mech. Eng.*, 1904, 1, 245.

their companions. The point of maximum velocity will shift from the center to a point nearer the opposing wall and will then slowly return to its normal position with a spiral movement. Solid particles on account of their greater mass may strike the opposing wall and if they or the wall are sticky may adhere there and build up deposits.

It will be evident, from what has preceded, that it will not be possible to find a single point in a gas main from which it is possible to draw a fair sample of gas for the determination of suspended solids. If a sample can only be taken at a single point, the termination of the sampling tube should be at about the point of mean velocity, as explained in the preceding section. In important tests it is advisable to draw a number of samples from various points in the cross-section of the main. A tube with numerous perforations along its length is useless for this work. Separate tubes should be used each with its own filter and aspirator as explained in Chapter I.

5. Velocity of Gas in a Sampling Tube.—The rate of flow through the sampling tube has a material effect on the accuracy of sampling as has also the inclination of the sampling tube to the gas stream. It is evident that if a sampling tube is inserted at A of Fig. 35 at right angles to the flow of gas, even assuming that the solid particles are uniformly distributed, the result will be incorrect for the heavy particles will tend to be carried past the open end of the tube and not drawn into it. The suspended solids will be reported low even if the speed of gas within the sampling tube is as high or even higher than that in the main. If, on the other hand, the opening of the sampling tube faces the approaching stream of solid particles as at B, on the same assumption of uniform distribution of particles, the result may be correct, or it may be high or low. If the speed of the gas in the sampling tube is the same as that in the main the result should theoretically be correct. The whole column of gas opposite the opening of the tube should enter without distortion. If, however, the

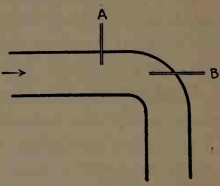

FIG. 35.—Diagram showing method of inserting sampling tube in gas main.

velocity in the sampling tube is lower than that in the main the column of gas approaching the opening will be disturbed and part of it will be forced aside. The solid particles will on account of their momentum not be pushed aside so readily and will therefore enter the tube in unduly great amount, giving a high result. If the velocity of the gas in the sampling tube is greater than that in the main there will again be a disturbance in the approaching column of gas. A column of gas larger than the opening of the tube will be sucked in, but the solid particles in the outer shell of gas thus sucked in will not be diverted from their course and will pass by the opening of the tube, giving a low result. Brady[1] states that in sampling blast-furnace gas an error of more than 44 per cent. was caused when the sampling speed was dropped to half that in the main. It is thus evident that the speed with which gas enters the sampling tube must be carefully controlled. The velocity of the gas must however be reduced before it passes through the filtering medium or the finely divided particles will not be taken out. The usual sampling tube has therefore a relatively small aperture. Care must be taken that the aperture is not so small that it will become clogged, which readily happens when tarry matters are present. Each case must be studied independently.

6. The Filtering Medium.—Where conditions permit, filter paper discs or shells make satisfactory filtering media. The Brady gas filter for dust in blast-furnace gas is described in the article referred to in the preceding section. A filter using a disc of filter paper as developed by Mr. W. S. Blauvelt[2] of the Semet-Solvay Company has been used by the author with good results.

When large amounts of tar are present a weighed tube filled with a fibrous material may with advantage be inserted ahead of the filter paper. The filtering materials to be inserted in the sampling tube will vary with conditions. If the temperature is high, sand or ignited asbestos is suitable. Ignited asbestos is usually to be preferred since on account of its fibrous nature it makes a more efficient and a lighter filter. This last consideration is of importance since the suspended solids collected frequently weigh only a few milligrams and it conduces to accuracy to have the increase

[1] *Jour. Ind and Eng. Chem.*, 3, 662 (1911).
[2] *Proc. Am. Gas. Inst.*, 4, 795 (1909).

in weight of the filter relative to its initial weight as large as may be. The tubes may be of glass, porcelain or quartz protected if desirable by an iron jacket. The tubes after filling and before use should be placed in an air bath heated to the temperature to which they are to be exposed later and dry air should be drawn through them until they are constant in weight. They should then be cooled in dry air, weighed, carefully stoppered and if possible kept in a dessicator until used. The asbestos for this purpose should not be soft enough to pack readily and choke the tube. The fine washed asbestos used for analytical work is not so good for this purpose as a cruder sort. Sometimes when much tar is present it is advantageous to procure the crude asbestos rock and merely crush it coarsely in an iron mortar.

7. Estimation of Suspended Tar and Water.—The amount of suspended matters caught by a filter paper may be estimated either by color or, if sufficient in amount, may be determined by weight. A second weight after drying at 105° C. for an hour will give by difference the moisture and other volatile matter, while the weight after ignition will give the mineral matter, correction being made if necessary for the change in composition due to ignition.

Where asbestos filters have been used a smiliar procedure may be followed provided the asbestos has been ignited before use. In drying the tube however it is not sufficient to heat it externally. Dry air must be drawn through until it comes to constant weight. The water will be driven off and also approximately 25 per cent. of the weight of the tar. The non-volatile tar remaining may afterward be extracted with chloroform or carbon bisulphide, and this figure increased by one-third will give a rough estimate of the amount of tar present. It is not possible to determine accurately the amounts of water and suspended tar since it is not feasible to determine how much of the material volatilized is tar and how much is water.

8. Electrical Precipitation of Suspended Particles.—Where the expense warrants the installation of the process, the method of electrical precipitation as developed on the large scale so successfully by Cottrell[1] may be applied. The equipment consists of a small step-up autotransformer capable of giving 15,000–30,000

[1] *Jour. Ind. and Eng. Chem.*, 3, 542, (1911).

volts, a rotating switch to rectify this high-tension alternating current and a precipitating vessel which may be made of an iron pipe with an insulated electrode in the center An exhauster for aspirating the gas and a meter for measuring it must also be provided. This apparatus will quantitatively precipitate all suspended solid and liquid bodies including tar and operates on such large amounts that the precipitated materials can readily be examined.

CHAPTER X

CHIMNEY GASES

1. Introduction.—A knowledge of the chemical composition of the gases escaping from a chimney aids much in controlling the efficiency of the furnace. It makes very little difference whether the fuel is burned to raise steam or to melt steel and it is of equally small importance whether the fuel burned be solid or liquid. The only assumption is that it is desirable to burn the fuel as completely as possible without the introduction of any unnecessary excess of air. When gaseous fuels are burned the same general principles apply but there is somewhat greater complication in calculation. This chapter therefore limits itself to a study of the gases arising from complete combustion of solid or liquid fuels. Let us see how much light a knowledge of the composition of the gas can throw on the operation of the furnace.

2. Formation of Carbon Dioxide.—Air is composed of practically 21 volumes of oxygen and 79 volumes of nitrogen and other inert gases. When oxygen unites with carbon there is formed carbon dioxide which is stable unless it comes into intimate contact with carbon or other reducing agent at a high temperature. Chemically the result is expressed as follows:

$$C + O_2 = CO_2.$$

The expression means not only that carbon dioxide is formed by the union of carbon and oxygen, but also indicates that *one volume of carbon dioxide is formed from one volume of oxygen* and that *the volume of the smoke gases after cooling is the same as that of the air which was used.* This follows from the law of Gay Lussac which states that a molecule of one gas occupies the same volume as that of any other gas under like conditions. The simplicity of this volume relation makes it extremely desirable to work with volumes instead of weights in problems where gases are involved.

Since one volume of oxygen forms one volume of carbon dioxide it follows that the theoretical best composition of the chimney gases from the combustion of carbon would be 21 per cent. CO_2 and 79 per cent. N_2. This is unattainable in practice because the strong reducing action of the glowing carbon on the carbon dioxide will cause formation of carbon monoxide (CO) which will not be again oxidized unless it is brought in contact with free oxygen while still at a high temperature. An excess of oxygen is in practice necessary to ensure this. It follows from the fact that the volume of the carbon dioxide is the same as that of the oxygen which formed it, that all chimney gases resulting from the combustion of pure carbon to carbon dioxide will contain 21 per cent. of CO_2+O_2 and 79 per cent. of N_2.

3. Effect of Hydrogen of Coal on Composition of Chimney Gases.—The simple relation stated in the preceding section only holds where carbon is the only fuel burned, a condition which is quite closely fulfilled with a coke fire and approximately fulfilled when anthracite coal is the fuel. When fuels contain notable percentages of hydrogen as does bituminous coal, and to a greater extent petroleum and most gaseous fuels, part of the oxygen of the air burns to water which escapes from the furnace as steam. When the gas is sampled for analysis part of this steam may condense. When the gas sample is stored over water it becomes fully saturated with water vapor so that its volume is independent of the amount of steam which it contained in the chimney and the result is the same as if the steam formed in combustion had all condensed and the gas had later become saturated with water vapor as happens, for instance, in the gas analysis apparatus. This is the assumption which is made in discussing combustion.

If, then, part of the oxygen of the air combines with hydrogen of the fuel to form steam which condenses to a liquid while the nitrogen associated with this oxygen remains as a gas, it is apparent that the percentage of nitrogen in the chimney gas must be more than the 79 per cent. present in the air. The extent of the change of volume may be readily calculated. Assume that an analysis shows 81 per cent. N_2. 100 cu. ft. of air contained 79 cu. ft. of nitrogen, which is now 81 per cent. of the chimney gas, therefore the volume of the gas is $\frac{79}{0.81} = 0.975$ or 97.5 per cent. of the initial

volume of air measured under the same condition of temperature and pressure. It follows that 2.5 of the 21 volumes of oxygen in 100 air have combined with hydrogen to form water.

The volume of the water formed, so long as it remains in the vapor form, will be twice that of the oxygen from which it was formed as shown by the equation

$$2H_2 + O_2 = 2H_2O.$$

The hydrogen in this case is contained in the coal and is considered as a solid just as the carbon is. In the case of gaseous fuels the problem is a little more complicated and is treated under Producer Gas.

4. Carbon Monoxide and Products of Incomplete Combustion.—The presence of carbon monoxide, hydrogen or hydrocarbons is a sign of incomplete combustion and represents loss of heat which would have been liberated in the furnace had combustion been complete.

Heating value 1 lb. C to CO_2	14,600 B.t.u.
1 lb. C to CO	4,450 B.t.u.

Since carbon burning to CO only evolves 30 per cent. of the heat obtainable by complete combustion it is evidently uneconomical to allow more than small amounts of this gas to appear in chimney gases.

It is frequently stated that carbon monoxide is formed when carbon burns with an insufficient supply of air. This is only a partial truth for with a bed of coals at a dull red heat it is difficult to form carbon monoxide no matter how much the air supply is limited. If the free oxygen in the chimney gases is below 3 per cent. it will be entirely normal to find products of incomplete combustion. The presence of carbon monoxide and other incompletely burned gases is abnormal when associated with much more than 3 per cent. free oxygen. It indicates either a faulty design of the furnace or carelessness on the part of the fireman. Furnaces intended for coal high in volatile matter must have roomy combustion chambers so that the streams of gas given off by the coal may have time to mix with air and burn before they become chilled by contact with cold surfaces. Furnaces designed for anthracite coal do not have such large combustion chambers and hence do not give good results with bituminous coal.

As mentioned in Chapter III, the estimation of carbon monoxide presents some difficulties and the careless analyst may readily report a fraction of a per cent. of carbon monoxide when none is there. On the other hand, the natural tendency is to fail to find hydrogen when it is present in only small amounts.

The presence of soot in chimney gases is not necessarily an indication that measureable amounts of unburned gases are present for the particles of tar and carbon formed by the destructive distillation of the coal burn much more slowly than do the gases and also have higher ignition temperatures and so are more likely to escape combustion.

5. Volume of Air and of Chimney Gases.—The volume of the air used in combustion per pound of carbon and the volume of the chimney gases may be calculated from the gas analysis. The method is based on the assumption that the nitrogen of the air passes through the furnace unchanged in volume, and that all of the nitrogen of the chimney gases is derived from the air. This assumption is practically correct, the small amount of nitrogen derived from the coal introducing only a negligible error.

It is necessary also to have some factor to connect the weight of carbon burned with the volume of the chimney gases. One pound of carbon burning to CO_2 requires 32.1 cu. ft. of oxygen measured wet at 60° F. and 30 in. barometric pressure and yields 32.1 cu. ft. carbon dioxide.

Let us assume the following gas analysis:

CO_2	8.5 per cent.
O_2	9.8 per cent.
N_2	81.7 per cent.

It was shown in § 3 that the increase in the percentage of the nitrogen over 79 was due to the condensation of steam formed by the union of hydrogen of the coal with oxygen of the air. The volume of these gases referred to 100 of air may be obtained by multiplying them by the factor $\frac{79}{81.7} = 0.966$.

$8.5 \times 0.966 =$	8.2	CO_2
$9.8 \times 0.966 =$	9.5	O_2
$81.7 \times 0.966 =$	78.8	N_2
	96.5	
O_2 which has disappeared as steam	3.5	forming 7.0 steam.
	100.0	

The volume of air used per pound of carbon may now be obtained.

To burn 1 lb. carbon $= 32.1$ cu. ft. O_2 forming 32.1 cu. ft. CO_2

Oxygen in excess $\frac{32.1 \times 9.5}{8.2} = 37.2$

Oxygen forming steam $\frac{32.1 \times 3.5}{8.2} = 13.7$

Total oxygen per pound carbon, 83.0 cu. ft.

Accompanied by $\frac{79}{21} \times 83.0 = 312.0$ cu. ft. N_2

Corresponding to 395.0 cu. ft. air.

The excess of air may be determined from the ratio

$$\frac{\text{Oxygen used}}{\text{Oxygen required}} = \frac{32.1+37.2+13.7}{32.1+13.7} = \frac{83.0}{45.8} = 1.8$$

The volume of the chimney gases is obtained directly from the above, it being remembered that the volume of the CO_2 is the same as that of the O_2 forming it and that the volume of the steam (assumed to be cooled to standard temperature without condensation) is twice the volume of the oxygen forming it.

Volume of chimney gases from 1 lb. carbon in the above example:

CO_2	32.1 cu. ft.
H_2O vapor 2×13.7	27.4 cu. ft.
O_2	37.2 cu. ft.
N_2	312.0 cu. ft.
Total chimney gases	408.7 cu. ft.

6. Loss of Heat in Chimney Gases.—The heat carried away by these gases may be determined by multiplying their volume by the rise in temperature and by their specific heat. It was first shown in 1883 by Mallard and LeChatelier that the specific heats of gases are not constant but increase with rising temperature. Engineers have been slow to adopt these variable specific heats but there can be no question as to their general correctness. The mean specific heats expressed in British thermal units per cubic foot and per pound at constant pressure have been calculated by the author from the most recent data of Holborn and Henning[1]

[1] *Annalen der Physik*, 23, 809 (1907).

and are given in Tables V and VI of the Appendix. It will be noted that the specific heats of oxygen, nitrogen and all permanent gases are the same per cubic foot, an agreement which holds true only for specific heats by volume and not for those for which the unit basis is weight.

The loss of heat per pound of carbon in the particular case given above will be calculated as follows, a temperature of 600° F. for the escaping gases being assumed:

Temperature through which gases are heated $600-60=540$.
Use mean specific heats from Table V corresponding to 600° F.

Heat lost in CO_2,	$32.1\times0.0253\times540$	= 439 B.t.u.
Heat lost in steam,	$27.4\times0.0221\times540$	= 328
Heat lost in oxygen, 37.2 Heat lost in nitrogen, 312	$349.2\times0.0177\times540$	= 3340 B.t.u.
		4107

It is necessary to know the percentage of carbon in the coal before this loss of heat per pound carbon can be calculated to the desired basis of loss per pound of coal.

The loss of heat per pound of dry coal =

$$\frac{\text{Loss per pound carbon} \times \text{per cent. carbon in dry coal}}{100}.$$

Moisture present in the coal when placed on the fire will be vaporized, and, in case combustion is complete, will escape from the stack as steam. It is immaterial whether or not it underwent decomposition in the fire, only the initial and final states being important. The amount of water thus vaporized calculated from the analysis of the coal is reported in pounds and is most conveniently kept in that form throughout the calculation. The mean specific heats by weight at constant pressure are given in Table VI of the Appendix. Moisture present in the air introduced into the firebox will be heated from room temperature to that of the escaping gases. Its amount may be determined from observations with a wet and dry bulb thermometer from which the percentage humidity may be calculated as described in § 14 of Chapter VII. The volume of water vapor per cubic foot of air for various temperatures is given in Table VII of the Appendix.

There is also steam in the stack gases which is derived from the union of the hydrogen and oxygen of the coal with each other. It is sufficiently accurate to assume that all of the oxy-

gen of the coal unites with the hydrogen of the coal to form water, that the excess or available hydrogen unites with the oxygen of the air to form water and that all of the carbon of the coal unites with the oxygen of the air to form carbon dioxide. The volume of steam due to this union of the hydrogen and oxygen of the coal with each other can only be accurately calculated from an ultimate analysis. Fortunately its amount is small and fairly constant for a given type of coal. The weight of water so formed, sometimes called "combined water," may be taken as:

2.5 per cent for anthracite coals.
6.0 per cent for Eastern bituminous coals.
10.0 per cent for bituminous coals of the Western or Illinois type.

These figures may for this purpose be added to the percentage of moisture in the coal.

There are also changes in the ash of the coal which may involve absorption of oxygen or liberation of SO_2 or CO_2 but they are negligible in a calculation of this sort.

PROBLEM ILLUSTRATING CALCULATION OF LOSS OF HEAT IN CHIMNEY GASES

Data	Coal as charged
Moisture	9.3 per cent.
Volatile matter	31.7
Fixed carbon	53.7
Ash	5.3
	100.0
B.t.u. per lb	12,456
Per cent. total carbon	71.6

Average composition of chimney gases	
CO_2	9.6 per cent.
O_2	9.0
N_2	81.4
	100.0
Temp. escaping gases	720° F.
Temp. inlet air	70° F.
Relative humidity	75 per cent.

VOLUME CHIMNEY GASES REFERRED TO 100 VOLUMES OF DRY AIR ENTERING FURNACE

$$\text{Factor} = \frac{79}{81.4} = 0.97$$

$9.6 \times 0.97 =$	9.3	CO_2
$9.0 \times 0.97 =$	8.7	O_2
$81.4 \times 0.97 =$	79.0	N_2
	97.0	
Oxygen which has disappeared to form H_2O vapor.	3.0	forming 6.0 H_2O
	100.0	

Volume chimney gases from 1 lb. carbon.

1 lb. carbon produces 32.1 cu. ft. CO_2. Factor $\frac{32.1}{9.3} = 3.45$

$9.3 \times 3.45 = 32.1$ cu. ft. CO_2
$6.0 \times 3.45 = 20.7$ cu. ft. H_2O vapor
$8.7 \times 3.45 = 30.0$ cu. ft. O_2
$79.0 \times 3.45 = 272.2$ cu. ft. N_2

Volume air required for combustion $100 \times 3.45 = 345$ cu. ft.
Moisture in air for combustion:

75 per cent. of saturation at $70° = 0.75 \times 0.026 = 0.019$ cu. ft. per cubic foot air.
$345 \times 0.019 = 6.56$ cu. ft. H_2O vapor in air for 1 lb. carbon.

Gases heated from $70° - 720° = 650°$ F.

Loss in CO_2 $= 32.1 \times 650 \times 0.0253$	$= 529$
Loss in H_2O $= 20.7 + 6.6 = 27.3 \times 650 \times 0.0221$	$= 392$
Loss in $O_2 + N_2 = 30.0 + 272.2 = 302.2 \times 650 \times 0.0177$	$= 3440$
B.t.u. lost in gases per lb. carbon burned	$= 4361$
B.t.u. lost in gases per lb. coal burned 4361×0.0716	$= 3122$

Moisture in coal 9.3 per cent	$= 0.093$ lbs.	per lb. coal.
Combined water in coal 6.0 per cent	$= 0.060$ lbs.	per lb. coal.
Total water with coal	$= 0.153$ lbs.	per lb. coal.

Heat absorbed in converting 1 lb. water to vapor at 70° F. = 1067. B.t.u.	
Heat absorbed in converting 0.153 lbs. water to vapor at 70° F. $= 0.153 \times 1067$.	$= 163$. B.t.u.
Heat absorbed in raising 0.153 lbs. water vapor from $70° - 720° = 0.153 \times 650. \times 0.4673$	$= 46$. B.t.u.
Total heat lost in water with coal	$= 209$. B.t.u.
Heat lost in gases per lb. coal	$= 3122$. B.t.u.
Heat lost in water per lb. coal	$= 209$. B.t.u.
Total heat lost per lb. coal burned	$= 3331$. B.t.u.

Per cent. heat lost $= \frac{3331}{12456} = 26.7$ per cent.

7. Interpretation of Analysis of Chimney Gases.—The conclusions indicated in the preceding paragraphs may be summarized as follows:

Carbon Dioxide.—The higher the percentage of CO_2 in chimney gases without the presence of CO or hydrocarbons, the more efficient is the furnace. When the fuel is coke or anthracite coal the sum of the percentages of carbon dioxide and oxygen should be between 20.5 and 20.8. If the fuel is bituminous coal the sum of the carbon dioxide and oxygen will drop to 19 per cent. and if the fuel is oil or gas the figure will be still smaller. In ordinary practice the percentage of carbon dioxide should be as large as the oxygen, and with well-equipped and operated plants the proportion of CO_2 to O_2 should be as high as 2 to 1. With liquid or gaseous fuels the proportion of CO_2 will be still higher.

The CO_2 as reported includes a small amount of SO_2 from the sulphur of the coal, which does not usually amount to more than a few hundredths of a per cent.

Oxygen.—When solid fuel is burned on an ordinary grate it is necessary to have an excess of air to insure complete combustion. This excess should be kept as small as possible.

Carbon Monoxide and Products of Incomplete Combustion.—These products should be entirely absent from chimney gases. Their presence indicates waste of fuel. Unless the analytical work is carefully done as much as 0.2 per cent. CO may readily be reported through error.

Nitrogen.—Nitrogen is present in air to the extent of 79 per cent. by volume and will be present in at least that percentage in chimney gases. With bituminous coal the percentage will rise to 81 per cent. and with oil or gaseous fuel the percentage will be higher. The percentage of nitrogen can only fall below 79 per cent. through the introduction of some gas which makes the total volume of the chimney gases greater than that of the air from which they were derived. The formation of carbon monoxide will affect this result since it occupies twice as much space as the oxygen from which it was derived. The amount of CO in chimney gases is, however, too small to exert any appreciable influence of this sort.

Loss of Heat in Chimney Gases.—The loss of heat will depend on the temperature and volume of the gases. The volume of the

gas is in general indicated by the relative percentage of carbon dioxide and oxygen. The higher the per cent. of oxygen and the lower the per cent. of carbon dioxide the greater is the loss of heat. The loss will vary in steam-boiler practice between 15 and 45 per cent. With smelting furnaces where the gases escape at high temperatures the loss may be much higher.

CHAPTER XI

PRODUCER GAS

1. Formation of Producer Gas.—Producer gas is formed whenever air is brought into contact with fuel under such conditions that carbon monoxide is an important constituent of the products resulting from their combination. The formation of producer gas is frequently said to be due to incomplete combustion, but the statement is only a half truth, for a limited quantity of air supplied to a fire will not necessarily produce carbon monoxide. The primary product formed when carbon burns in air is carbon dioxide, the equation being written

$$C+O_2=CO_2$$

If this carbon dioxide comes into intimate contact with glowing carbon, it unites with more carbon and carbon monoxide is formed according to the equation

$$CO_2+C\rightleftarrows 2CO.$$

These two reactions are frequently combined into one and the typical reaction of the gas producer is usually written

$$2C+O_2=2CO.$$

This equation shows that one volume of oxygen is converted into two of carbon monoxide. The composition of the resulting gas may be shown as follows:

$$100 \text{ air} = \begin{cases} 21O_2 = 42CO = 34.7 \text{ per cent. CO.} \\ 79N_2 = 79N_2 = 65.3 \text{ per cent. } N_2. \end{cases}$$

When steam is introduced in the bottom of the producer the reaction desired is:

$$C+H_2O=CO+H_2.$$

If the temperature of the producer is low, this reaction may proceed in part as follows:

$$C+2H_2O=CO_2+2H_2.$$

If bituminous coal is placed in the producer there will also be products of destructive distillation including hydrocarbons both saturated and unsaturated, hydrogen and carbon monoxide.

The largest single constituent of producer gas is nitrogen, which will not often fall below 50 per cent. Carbon monoxide and hydrogen rank next in percentage. The hydrocarbons are practically always under 5 and are usually less than 3 per cent. Carbon dioxide should be low. It is, however, frequently as high as 10 per cent.

The following are some typical analyses of producer gas.[1]

TYPICAL ANALYSES OF UP-DRAFT PRESSURE-PRODUCER GAS

(Per cent. by volume)

	From Bituminous Coal	From Lignite	From Peat
Carbon dioxide (CO_2)	9.84	10.55	12.40
Oxygen (O_2)	.04	0.16	0.00
Ethylene (C_2H_4)	.18	0.17	0.04
Carbon Monoxide (CO)	18.28	18.72	21.00
Hydrogen (H_2)	12.90	13.74	18.50
Methane (CH_4)	3.12	3.44	2.20
Nitrogen (N_2)	55.64	53.22	45.50

TYPICAL ANALYSES OF DOWN-DRAFT PRODUCER GAS

(Per cent. by volume)

	From Bituminous Coal	From Lignite	From Peat
Carbon dioxide (CO_2)	6.22	11.87	10.94
Oxygen (O_2)	0.13	0.01	0.41
Ethylene (C_2H_4)	0.01	0.00	0.06
Carbon monoxide (CO)	21.05	16.01	16.91
Hydrogen (H_2)	12.01	14.76	10.19
Methane (CH_4)	0.49	0.98	0.66
Nitrogen (N_2)	60.09	56.37	60.83

[1] From Bulletin 13, U. S. Bureau of Mines. "Résumé of Producer-Gas Investigations by R. H. Fernald and C. D. Smith.

2. Sampling Producer Gas.—The quality of gas yielded by a given producer may change quickly. Soon after a charge of bituminous coal has been added, the amount of volatile tarry vapors and of gaseous hydrocarbons in the gas increases. Within a half hour the larger part of the volatile matters may have distilled off leaving the gas almost free from hydrocarbons and from tar vapors. Rapid changes will also be noted after poking the fire.

An average sample of producer gas may be obtained only by extending the sampling over a long period, as directed in Chapter I. There will be especial difficulty in determining the quantity and heat value of the suspended tarry particles. Yet these values must be ascertained if the heat value of the crude gas is to be determined accurately. The method of collecting the tar particles on filter papers, given in Chapter IX, may be followed and the weight of tar per cubic foot of gas thus obtained. The papers and tar may then be burned in a bomb calorimeter and after deduction of the heat due to the known amount of filter paper, the heating value of the tar may be obtained. This determination is not often made, as it is difficult to carry it out accurately. However, it is not possible to find the true heat balance on a furnace fired with crude producer gas, especially if from a bituminous producer, unless such a determination is made.

Ordinarily the determination of tar and suspended particles is neglected and the sampling then is to be conducted as described in Chapter I.

3. Analysis of Producer Gas.—The constituents to be determined in producer gas are carbon dioxide, unsaturated hydrocarbons, oxygen, carbon monoxide, hydrogen and methane. The methods are given in Chapters II, III and IV. No difficulty will be experienced except with hydrogen and methane. The percentage of these gases, except in water gas, is usually so small that a sample after removal of the absorbable constituents is no longer explosive when mixed with air. It should be emphasized that failure to obtain an explosion does not mean the absence of hydrogen and methane but merely that they are present in less than explosive amounts. Explosion may be brought about by addition of a known volume of pure hydrogen to form an explosive mixture but it is usually simpler to use a method which

does not involve explosion. Combustion with a hot platinum spiral as in the Dennis and Hopkins method (§ 9 of Chapter IV) or with copper oxide as in the Jaeger method (§ 11 of Chapter IV) affords a satisfactory method for determination of these constituents.

4. Interpretation of Analysis.—The important constituents are carbon dioxide and carbon monoxide. Oxygen should be entirely absent, as it should all have been brought into combination in its passage through the producer. Its presence in a producer gas may be an indication of leakage in sampling or of leakage into the flue prior to sampling. Rarely, if operating conditions in the producer are bad, and the fire is thin may, there be such a channel formed in the producer that air will rush through the producer without its oxygen becoming combined. Such a condition will be indicated by extremely high carbon dioxide, with low percentages of combustible gases. When a producer is running under normal conditions its operation may be quite closely checked by the percentage of carbon dioxide alone. High carbon dioxide is in practically all cases an unfavorable symptom. It may be due to a cold fuel bed in the producer caused either by an excess of steam or by slow running, it may be due to a thin fuel bed which does not allow sufficient time and contact for the reduction of the carbon dioxide to monoxide, and it may be due to channels or chimneys in a deep fire which allow uncombined air to get through the fuel bed and burn above the coals.

A cold fuel bed in a producer burning bituminous coal will tend to increase the percentage of unsaturated hydrocarbons, but in no case will they amount to more than a few tenths of a per cent. A hot and thin fuel bed and especially a channeled fuel bed will cause the unsaturated hydrocarbons to practically disappear, since they are decomposed at the high temperature and of all the gases show the greatest avidity for oxygen.

The carbon dioxide is almost a direct measure of the thermal efficiency of the producer, the only exception being its appearance as the result of the interaction of carbon and steam at a relatively low temperature as in the Mond producer where it is accompanied by a high percentage of hydrogen. Under other circumstances high carbon dioxide means low thermal efficiency

for the 70 per cent. of the energy of the carbon which should have been converted into the potential energy of the carbon monoxide is all changed to the sensible heat of the carbon dioxide and accompanying gases.

5. Heating Value of Producer Gas.—The heating value of producer gas may be determined in a calorimeter as described in Chapter VII for illuminating gas. A special tip must be used on the burner and care be taken to see that the flame burns clear. The heating value of producer gas may be as low as 100 British thermal units per cubic foot and it frequently happens that it does not burn readily in a Bunsen burner. The gas must be carefully cooled and cleaned before testing. This operation separates tar whose amount and heat value must be determined as directed in § 2 of this chapter. The heating value of the purified gas may also be calculated from the analysis as indicated in § 17 of Chapter VII. The low percentage of unsaturated hydrocarbons in producer gas makes the errors of calculation less than is the case with illuminating gas. On account of the difficulty in cleaning the gas and in keeping a steady flame in the calorimeter, the heating value is usually obtained by calculation.

It is worth while to emphasize again that the heating value of the cleaned gas from bituminous coal is lower than that of the hot gas which still contains tar vapors and that allowance must be made for the tar vapors in calculating the heat value of the gas which is used while hot.

6. Volume of Producer Gas.—It would be very desirable to be able to calculate the volume of producer gas per pound of coal, as is done in Chapter X for chimney gases. There are, however, so many possible reactions in the gas producer and the changes in volume are so complicated, especially in a bituminous producer, that it is only possible to make such calculations for simple cases.

Assume a producer burning pure carbon in dry air. It is manifest that the only products of combustion will be CO_2,CO and N_2 Assume the following composition of the gas

CO_2	5.5 per cent.
CO	25.6 per cent.
N_2	68.9 per cent.

The air entering the producer was composed of 79 volumes of nitrogen for every 21 volumes of oxygen. The change in percentage of the nitrogen in the producer gas is due to changes resulting from the union of oxygen with carbon. The first step is to trace the changes taking place when 100 volumes of air pass through the producer and find the relative volumes of CO_2 and CO for 79 volumes of N_2.

$$\begin{aligned}
CO_2 \quad 5.5 \times \frac{79}{68.9} &= 6.3 = 6.3 \text{ vols. } O_2 \\
CO \quad 25.6 \times \frac{79}{68.9} &= 29.4 = 14.7 \text{ vols. } O_2 \\
N_2 \quad 68.9 \times \frac{79}{68.9} &= 79.0 = 79.0 \text{ vols. } N_2 \\
&\qquad\qquad 100.0 \text{ vols. air.}
\end{aligned}$$

One pound of carbon burning to carbon dioxide requires 32.1 cu. ft. of oxygen (at 60° F. and 30 in. of mercury pressure) and yields 32.1 cu. ft. of carbon dioxide. One pound of carbon burning to carbon monoxide requires 16.05 cu. ft. of oxygen and yields 32.1 cu. ft. of carbon monoxide. It follows that the weights of carbon burning to CO and CO_2 are proportional to the volumes of the two gases. In the present instance

$$CO_2 \quad 6.3 = \frac{6.3}{35.7} \times 100 = 17.7 \text{ per cent.}$$

$$CO \quad \frac{29.4}{35.7} = \frac{29.4}{35.7} \times 100 = 82.3 \text{ per cent.}$$

One pound of carbon yields

$$\begin{aligned}
0.177 \times 32.1 &= 5.7 \text{ cu. ft. } CO_2 \\
0.823 \times 32.1 &= 26.4 \text{ cu. ft. CO} \\
3.76 \times 32.1 &= 120.7 \text{ cu. ft. } N_2 \\
&\qquad 152.8 \text{ cu. ft. producer gas.}
\end{aligned}$$

The sensible heat will be calculated as in Chapter X.

$$\begin{aligned}
5.7 \times 0268 \times 1000 &= 153 \text{ B. t. u.} \\
26.4 & \\
120.7 & \\
147.1 \times 0180 \times 1000 &= 2647 \text{ B. t. u.} \\
&\qquad 2800 \text{ B. t. u.}
\end{aligned}$$

Energy in 26.4 cu. ft. of CO	8534 B. t. u.
Sensible heat in gases	2800 B. t. u.
Total energy in gas at 1000° F.	11334 B. t. u.

Efficiency of producer when gas is used at

$$1000° \text{ F.} = \frac{11334}{14600} \times 100 = 77.6 \text{ per cent.}$$

7. Efficiency of a Gas Producer.—In the simple instance cited above it is easy to calculate the energy contained in the gas. The only potential energy in the gas from one pound of carbon is contained in the 0.823 lb., which is now in the form of 26.4 cu. ft. carbon monoxide. The heating value of this is:

$$26.4 \times 323.5 = 8534 \text{ B.t.u.}$$

The total energy of the coal if burned to carbon dioxide would be 14600 British thermal units. If the gas is cooled before being burned so that its only energy is the potential energy of the carbon monoxide the efficiency of the producer is

$$\frac{8534}{14600} \times 100 = 58.4 \text{ per cent.}$$

If the gas is burned while still hot, say at 1000° F., there should be credited to the producer also the sensible heat of the gas, as calculated in the preceding section where the efficiency was shown to be 77.6 per cent.

The above simple relations do not hold when steam is being injected into the producer with the air nor when bituminous coal is being used as a fuel. On account of the varied possibilities of chemical reaction in these cases the volume of the gases cannot be calculated from their chemical composition. If the volume of the gases is measured by a Venturi meter, or otherwise, then it is possible to calculate the sensible and potential energy of the gases as indicated in this chapter and the one preceding.

CHAPTER XII

ILLUMINATING GAS AND NATURAL GAS

1. Introduction.—Chemical analysis plays a minor rôle in testing illuminating gas and natural gas. The determination of heating value is described in Chapter VII and of candle-power in Chapter VIII. The ordinary chemical analysis as described in Chapters III and IV usually includes the determination of carbon dioxide, unsaturated hydrocarbons, oxygen, carbon monoxide, hydrogen and methane, nitrogen being taken by difference. A separate determination of benzene is sometimes desired in illuminating gas and of gasoline vapors in natural gas. Sulphur may be called for in both gases. Napthalene and ammonia are frequently determined in coal gas.

2. Sampling.—The sampling of natural gas and of purified illuminating gas usually offers little difficulty, since the gases are thoroughly mixed and contain such small amounts of suspended particles that they are usually negligible. The chief point to be observed in sampling from service pipes in cities is to see that the gas is allowed to run long enough to flush out the pipe and bring to the sampling cock gas which is representative of that flowing in the mains. Illuminating gas of high candle-power must not become chilled in the sampling process, for there is danger of condensing the benzene or other hydrocarbon vapors which it contains. Rubber connections are also to be minimized in sampling because of the solubility of the hydrocarbons in rubber. The water used in the sampling vessels must be carefully saturated before use, because unsaturated hydrocarbons are relatively soluble in water.

In case unpurified illuminating gas is to be sampled, additional precautions must be taken an account of the presence of material amounts of ammonia, hydrogen sulphide, carbon dioxide and other very soluble gases, as well as suspended tar particles. In case it is sufficient to determine what the approximate composition of the gas would be after purification it is sufficiently accu-

rate to sample in the usual way and trust the water of the sampling tank to remove the ammonia, hydrogen sulphide and part of the carbon dioxide. In case the actual composition of the unpurified gas is desired, these soluble constituents must be separately determined as indicated in succeeding sections.

3. General Scheme of Analysis.—Carbon dioxide, unsaturated hydrocarbons, oxygen, carbon monoxide, hydrogen and methane are usually determined according to the methods of Chapters III and IV. In the case of unpurified illuminating gas there may be appreciable amounts of hydrogen sulphide absorbed with the carbon dioxide. If it is desired to separate the two the hydrogen sulphide may be estimated according to the method of § 6. The estimation of carbon dioxide, oxygen and carbon monoxide does not present any peculiarities, although emphasis should be laid on the necessity of complete removal of the unsaturated hydrocarbons before the estimation of oxygen by phosphorus. In the case of Pintsch gas it sometimes requires five minutes' shaking with bromine water to affect such a complete removal of the hydrocarbons that the phosphorus will smoke when the gas is subsequently passed over it. The determination of hydrogen and methane in illuminating gas offers no marked peculiarity. In natural gas, vapors of the gasolines may be present and complicate the calculation. Ethane may also be present in natural gas and also in water gas and Pintsch gas. The methods for its determination have been discussed in Chapter IV. Nitrogen is taken by difference and as the analysis is a rather long and complicated one, the errors piling up on the nitrogen are apt to be material. A direct combustion of the gas with copper oxide, as described in § 12 of Chapter IV, gives a more accurate determination of the residual nitrogen.

4. Chemical Composition of Illuminating Gas.—The so-called "coal gas" is made by the destructive distillation of coal in closed retorts. The composition of the gas is dependent on the composition of the coal, the temperature of the retort and to some extent its shape and size. There is nothing, however, which distinctly characterizes gas from the large retort of the by-product coke oven from that of the small horizontal retort of the gas works. The oxygen of the coal appears in the gas partly as carbon dioxide, partly as carbon monoxide, and partly as water vapor.

None of it will be evolved as gaseous oxygen. The carbon monoxide will be greater at a high temperature than at a low one, but will usually stay between the limits of 5 and 9 per cent. A high retort temperature will cause cracking of the hydrocarbons with decrease of their percentage and increase of hydrogen. A fraction of 1 per cent. of free oxygen is normally present in illuminating gas, partly because of air entering during the operation of charging and drawing the retort, partly because of leaks in the long condensing system and partly because of liberation of the oxygen dissolved in the water used in the scrubbers. In so far as this oxygen comes from the air it must be accompanied by four volumes of nitrogen. Nitrogen must always be present in this amount. Less than four volumes of nitrogen for one of oxygen indicates a faulty analysis. The unavoidable nitrogen in the gas arising from the destructive distillation of the nitrogenous compounds of the coal will be between 1 and 1 1/2 per cent. High percentages of nitrogen unaccompanied by a corresponding amount of oxygen indicate that suction has been maintained on the porous retorts, so that air has been sucked in. The oxygen thus brought in contact with the hot gas will at once burn with formation of carbon dioxide or water while the nitrogen will remain and appear as such in the purified gas. In the manufacture of water gas a high percentage of nitrogen will result if the gasmaker turns the gas into the holder before all the gas produced while blowing air is flushed from the machine by the water gas.

TYPICAL ANALYSES OF ILLUMINATING GAS

	1	2	3	4	5
C_6H_6	*	1.2	0.2	*	1.3
CO_2	1.5	1.4	1.3	2.7	3.5
CnH_{2n}	4.6	4.0	2.0	6.5	11.6
O_2	0.3	0.9	0.5	1.1	0.7
CO	7.1	4.6	4.8	12.4	31.6
H_2	46.4	49.6	50.7	38.4	35.7
CH_4	36.3	35.0	38.1	28.4	9.0
N_2	3.7	3.3	2.4	10.5	3.7
					C_2H_6 2.9

* Not separately reported.

1. Coal gas of 17 c.p. and 650 B.t.u.

2. Coke oven gas enriched by benzol to 16.4 c.p. and 626 B.t.u. (*Proc. Am. Gas Inst.*, 6, 519 (1911).)

3. Coke Oven Gas. Fuel Gas (*Proc. Am. Gas Inst.*, 6, 519 (1911).)

4. Mixed Coal and Water Gas 15 c.p. and 615 B.t.u.

5. Carbureted Water Gas of 24 c.p. and 649 B.t.u. (*Proc. Am. Gas Inst.*, 7, 739 (1912).)

5. Benzene.—Benzene is a normal constituent of coal gas and also probably of water gas, but its amount in unenriched gases is always less than 1 per cent., and it is not usually determined. Its solubility in water and in caustic soda is slight so that in the ordinary analysis the benzene is not absorbed by the caustic but passes on to the bromine pipette where it dissolves in the ethylene bromide formed in the reaction between ethylene and bromine and is therefore estimated with the ethylene as "illuminants." As benzene has a very high illuminating power this grouping is logical and sufficiently satisfactory for most purposes.

Hempel recommends that 1 c.c. of absolute alcohol be placed in a pipette otherwise filled with mercury. An explosion pipette answers well for this purpose. A sample of gas is to be passed into the pipette and shaken with the alcohol to saturate it with ethylene, and the sample to be analyzed is later passed into this same pipette and shaken three minutes. The gas is then drawn back into the burette and passed into a second mercury pipette containing 1 c.c. of distilled water which removes the alcohol vapors. The decrease in volume from the initial reading is recorded as benzene. The method is to be considered only an approximate one.

Morton[1] recommends that, after removal of carbon dioxide by caustic soda as usual, the gas be passed into an ordinary simple absorption pipette containing concentrated sulphuric acid (sp. gr. 1.84) and shaken *vigorously* for one minute. The decrease in volume after drawing back into the burette represents benzene. Dennis and McCarthy[2] dispute the accuracy of this method and propose ammoniacal nickel cyanide as a reagent. Their directions for preparation of the reagent are as follows:

[1] *Jour. Am. Chem. Soc.*, 28, 1728 (1906).

[2] *Jour. Am. Chem. Soc.*, 30, 233 (1908).

"To 50 grm. of nickel sulphate ($NiSO_4.7H_2O$), dissolved in 75 c.c. of water, are added 25 grm. of potassium cyanide dissolved in 40 c.c. of water. After the addition of 125 c.c. of ammonium hydroxide (sp. gr. 0.91) the mixture is shaken until the nickel cyanide has completely dissolved and is then allowed to stand at a temperature of 0° for twenty minutes. The clear liquid is decanted from the crystals of potassium sulphate that have been precipitated, and is treated with a solution prepared by dissolving 18 grm. of crystallized citric acid in 10 c.c. of water. After the mixture has stood again at 0° for ten minutes, the greenish-blue supernatant solution is decanted and is introduced into a gas pipette. Two drops of liquid benzene are now added to the reagent through the large tube of the pipette and the pipette is shaken until the benzene has combined with the reagent. This is effected in two or three minutes. This addition of benzene to the reagent is made because it was found that at times a freshly prepared solution of the ammoniacal nickel cyanide did not quantitatively remove benzene vapor until it had been used for four or five determinations and had absorbed some of the substance."

The gas after carbon dioxide has been removed by caustic is passed into the pipette containing the ammoniacal nickel cyanide solution and drawn back and forth between the burette and pipette for about two minutes. It is then passed into a five per cent. solution of sulphuric acid and shaken until the ammonia is absorbed, which requires about two minutes. According to the authors, the absorption is quantitative and the result unaffected by ethylene.

The process of Haber and Œchelhaüser[1] is based on Bunte's observation of the solubility of benzene in ethylene bromide. The authors treat the gas with a fresh solution of bromine water to which is added, immediately after the reaction, an excess of strong potassium iodide. The liberated iodine is titrated with thiosuphate and the difference between the figures of this titration and those obtained by a blank test on an equal volume of the original solution represents the bromine which has combined with the ethylene. One cubic centimeter decinormal thiosulphate corresponds to 1.12 c.c. ethylene at 0° C. and 760 mm. or to 1.22 c.c. at 60° F. and 29.5 in. mercury pressure. The diminution in volume of the gas after the usual treatment with bromine water followed by caustic gives the

[1] *Jour. für Gasbel.*, 43, 347 (1900).

sum of the benzene and ethylene. The difference between this volume and that indicated by the titration for ethylene gives the benzene.

If a more exact method of estimation of benzene is desired and a large sample of gas can be obtained the method of Harbeck and Lunge[1] may be used. It consists in aspirating 10 liters of the gas through a mixture of equal weights of fuming nitric acid and concentrated sulphuric acid. Part of the resulting dinitrobenzene crystallizes out after the acids are diluted, cooled and neutralized, and may be filtered and weighed. The dinitrobenzene remaining in solution is extracted from an aliquot portion of the filtrate with ether and also weighed.

6. Hydrogen Sulphide.—Hydrogen sulphide should be present only in minute traces in purified illuminating gas. The usual test is an approximate one based on the reaction of hydrogen sulphide and lead acetate to form black lead sulphide. A strip of white filter paper moistened with colorless lead acetate is exposed to the gas and the depth of the resulting black stain noted. The details of the test differ widely. The New York State Commission prescribes that gas shall show no hydrogen sulphide when tested by exposing the paper moistened with lead acetate to a current of gas burning at the rate of 5 cu. ft. per hour. The paper must not become discolored after thirty seconds of such exposure. Ramsburg[2] has given a full discussion of the various methods of testing for hydrogen sulphide in purified gas.

Hydrogen sulphide is always present in unpurified illuminating gas. In the ordinary gas analysis it is absorbed by the caustic soda simultaneously with the carbon dioxide and reported with it. Its quantitative estimation may be carried out as follows. One or more liters of the gas is bubbled through a solution of ammoniacal cadmium chloride and the resultant cadmium sulphide is filtered. If the precipitate contains much tar it may be washed on the filter with benzol. Place filter and precipitate in cold dilute hydrochloric acid till dissolved and titrate with standard iodine. If the iodine solution is made by dissolving 1.0526 grm. iodine to the liter, 1 c.c. will be equivalent to 1/10

[1] *Zeit. für anorg. Chem.*, 16, 41 (1898).

[2] *Proceedings Am. Gas. Inst.*, 4, 453, 1909.

c.c. of hydrogen sulphide measured damp at 60° F. and under 30 in. of mercury pressure. A solution of ten times the above strength is more convenient if much hydrogen sulphide is present.

A rapid approximate estimation of hydrogen sulphide may be made in the Bunte gas burette described in § 4 of Chapter V. The burette is first filled with water containing a little thin starch paste to act as indicator, and the sample of gas drawn in and measured rapidly to prevent error due to the solubility of the hydrogen sulphide in the water of the burette. Standard iodine solution is now admitted from the reservoir at the top of the burette, about a cubic centimeter at a time, until the blue color formed by the reaction between the iodine and starch persists after repeated shaking, showing that the hydrogen sulphide has all been oxidized. If iodine solution of the concentration given above has been used, the volume of hydrogen sulphide may be read directly from the volume of iodine used, which must be obtained by measuring the iodine solution still remaining in the reservoir of the burette. Tutwiler has modified the burette by making the reservoir longer and graduating it so that the iodine used may be read directly.

7. Total Sulphur Compounds.—Illuminating gas and almost all other gases used for fuel contain, in addition to hydrogen sulphide, compounds of sulphur and carbon such as carbon bisulphide and more complex compounds like the mercaptans. These compounds are usually estimated after complete combustion in which process all the sulphur, whatever its previous combination, is converted into sulphur dioxide and sulphur trioxide. These gases are absorbed, oxidized to sulphuric acid and weighed as barium sulphate. Care must be taken to see that the air used for combustion, which is usually ten times the volume of the gas, is itself free from sulphur compounds, and that combustion is complete. The form of burner and absorption apparatus is immaterial, except for convenience. The most usual form is that of Drehschmidt which is illustrated in Fig. 36. Harding[1] and Jenkins[2] have both described modifications of the apparatus which may be made from ordinary laboratory apparatus by anyone with some skill in blowing glass.

[1] *Jour. Am. Chem. Soc.*, 28, 537 (1906).
[2] *Jour. Am. Chem. Soc.*, 28, 542 (1906).

In the Drehschmidt apparatus the gas is measured in an experimental meter and burned in a Bunsen burner which is enclosed in a metal case and is supplied with air which has been purified by passing through a tower A in contact with dilute caustic soda. The metal case surrounding the burner terminates at the level of the burner top and is continued as a glass chimney drawn down at the top and terminating in a tube leading to a train of absorption bottles. The construction of the apparatus is readily evident from the cut.

In making a test about 25 c. c. of dilute Na_2CO_3 (approximately

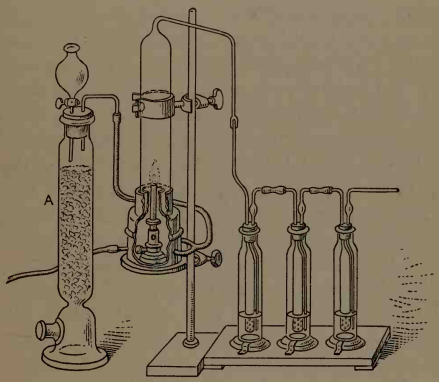

FIG. 36.—Drehschmidt's sulphur apparatus.

5 per cent.) is poured into each of the absorption cylinders and to the first two are added a drop or two of bromine to oxidize the SO_2 vapors. The train is then connected to an aspirator. The burner itself is removed from the case, lighted and adjusted to a consumption of about 1 cu. ft. of gas per hour. The aspirator is then started and adjusted so that the air bubbles rapidly through the absorption train and the lighted burner is slipped into its case where it fits snugly. If all the adjustments are properly made the gas continues to burn with a clear blue flame and the products of combustion are sucked into the absorption train where the SO_2 formed in combustion is absorbed and oxi-

dized to Na_2SO_4. The proper adjustment of the flow of air to keep the burner alight offers difficulties to the beginner which only practice can overcome. After 1 cu. ft. of gas has been burned, the burner is removed from the casing and any moisture which has condensed in the glass chimney is rinsed into the carbonate from the absorption vessels. The carbonate is acidified with HCl, boiled and treated with $BaCl_2$ in the usual manner to precipitate the sulphate. 1 grm. $BaSO_4 = 0.1373$ grm. S. or 2.119 grains S. The result is usually reported as grains sulphur per 100 cu. ft. of gas measured under standard conditions.

8. Napthalene.—The amount of the hydrocarbon, napthalene $C_{10}H_8$, usually present in gas is less than one-tenth of 1 per cent. Its small amount would make it unworthy of consideration were it not for its disagreeable property of causing stoppages in gas mains. Its estimation is therefore sometimes demanded as one of the steps in controlling the manufacturing process.

The usual method for purified gas is that devised by Coleman and Smith[1], who based their method on Küster's[2] method for separating napthalene from other hydrocarbons. The method depends upon the property which napthalene possesses of combining molecule for molecule with picric acid to form an insoluble compound. In the author's laboratory it has been customary to make the picric acid about 1/20 normal, which is an almost saturated solution, and to use as alkali $Ba(OH)_2$ 1/5 normal, with phenolphthalein or lacmoid as indicator. The color change is not difficult to observe, but the same conditions must always be observed in the analysis that are maintained in the standardization. When the gas to be tested has been purified and there is no danger of napthalene deposition at room temperature the gas may be passed through a wet experimental meter, then through a wash bottle containing dilute tartaric or other non-volatile acid to remove all traces of ammonia, then through a bottle containing water to stop acid which might have spattered over and then through a bulbed gas washing tube with about ten bulbs containing 50 c.c. of the standard picric acid. A yellow precipitate betrays the presence of napthalene. After five or more cubic feet of gas have been bubbled through the apparatus, the

[1] *Jour. of Gas Lighting*, 75, 798 (1900); 80, 1277 (1902).
[2] *Berichte*, 27, 1101.

bulbed tube is disconnected and washed into an Erlenmeyer flask of about 150 c.c. capacity, the bulbed tube being rinsed with 50 c.c. of picric acid from a pipette. The flask is then closed with a rubber stopper carrying a glass tube through which most of the air is sucked from the flask by a filter pump in order that it may not blow up when heated later. The evacuated flask is then placed in a water bath which is maintained at the boiling temperature for an hour. Rutten[1] says that it is sufficient to heat to 40° C. for half an hour. The flask is then removed and allowed to cool when the naphthalene picrate will have recrystallized as a definite compound $C_{10}H_8$. $C_6H_2OH(NO_2)_3$. This is filtered off and an aliquot part of the filtrate is titrated with alkali. The difference between the amount of alkali required for this titration and that which would have been required on a blank titration gives, when calculated for the whole volume of picric acid present, the naphthalene absorbed. One cubic centimeter of N/5 $Ba(OH)_2$ is equivalent to 0.0256 grm. naphthalene. If great accuracy is not required the heating of the naphthalene picrate in its solution may be dispensed with.

When gas freed from tar particles but otherwise unpurified is to be tested for naphthalene, it must be freed from ammonia and hydrogen sulphide, which affect the titration. The gas must not be allowed to cool below the temperature of the main during this purification process or naphthalene may deposit. The purifying train may be placed in an oven such as that shown in Fig. 38, placed so that it is in close proximity to the main and heated to the desired temperature. The first washer may contain lead acetate, the second a dilute acid and the third water. The tube with picric acid must not be placed in the oven since naphthalene will not be absorbed by a warm solution, but must be immediately outside. If naphthalene is deposited in the glass connecting tube it may be vaporized and driven forward by heat. Where much naphthalene is present two bulbed tubes should be used in series and if much precipitate appears in the second tube the liquid in the first tube should be renewed since a dilute solution of picric acid does not remove naphthalene completely. The precipitated naphthalene is estimated in the same manner as in the case of purified gas.

[1] *Jour. für Gasbel*, 52, 694 (1909).

Where naphthalene must be estimated in crude gas still containing suspended tar and it is desired to separate the naphthalene present as vapor in the gas from that which is carried in the dissolved tar particles, the method becomes still more complicated. The method devised by the author[1] to separately determine the naphthalene present as vapor in the gas from that which is carried in the dissolved tar particles involves precipitation of naphthalene as the picrate with subsequent recovery of the naphthalene. Considerable care is necessary in sampling gases which contain tar, if it is desired to distinguish between the naphthalene actually present as vapor in the gas and that existing dissolved in the fine, mist-like particles of tar suspended in the gas and which will be removed later by mechanical scrubbing. It is out of the question to collect a tank of gas, say from the foul main, and transport it to the laboratory for examination. The condensation and separation of tarry products in the gas holder would nullify the value of the figures obtained. It is necessary to separate the suspended tar and remove the naphthalene before change of temperature has had time to alter the conditions prevailing at the point of sampling. This requires that the tar vapors shall be mechanically filtered from the gas without any change in temperature. The result is attained by inserting horizontally into the main a glass tube about 1/2 in. in diameter filled with glass wool or asbestos fiber. This tube should project into the main at least 6 in. and at as short a distance outside the main as possible should connect with the picric acid absorbing train, and then with a gas holder of about 1 cu. ft. capacity and of known volume as shown in Fig. 2 of Chapter I. The strong solvent power of tar for naphthalene renders it absolutely essential that the gas shall not be scrubbed by passing through cold tar, as would be the case if the tube for separation of the tar were placed outside the main and, for example, connected to a pet cock. After the sample has been drawn, the picric acid contains the naphthalene and tar which were still present in the gas as vapor. The solution and precipitate is washed into a 200 c.c. Erlenmeyer flask and treated with alkali to neutralize the picric acid. It is our custom to add here an excess

[1] *Proc. Mich. Gas. Ass.*, 1904; 1905, 83.

of solid alkali, making an almost saturated solution when hot, merely to prevent so much moisture being carried into the drying tube. As this addition of solid alkali makes the solution hot, it should not be added until just before the apparatus is connected up so as to avoid loss of naphthalene. If the glass connecting tube contains naphthalene deposited from the gas by condensation the tube should be broken into fragments and dropped into the same flask.

The flask is then corked with a stopper carrying two glass tubes, one long enough to reach nearly to the bottom of the flask and the other terminating just below the cork and extending above the cork to make connections to the tube containing

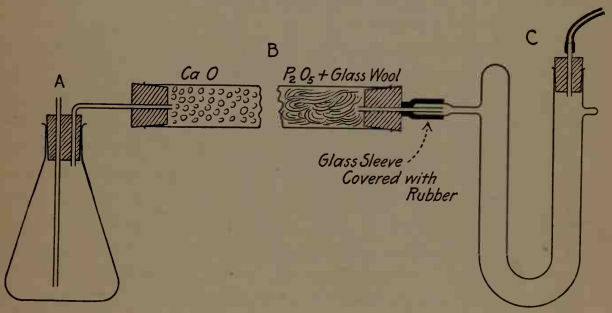

FIG. 37.—Details of naphthalene train.

lime and phosphorus pentoxide as shown at A of Fig. 37. At the other end of the drying tube B close connection is made to a small weighed U tube C which can be immersed in ice water. The tube containing the asbestos and tar is connected directly to a similar drying tube and U tube. The arrangement of the train is shown in Fig. 37 and the whole set in the oven is shown in Fig. 38. The oven is heated to 70°–80° C. and air slowly drawn through the system, volatilizing the naphthalene and moisture in the tar. The moisture is taken up by the dryer—lime and phosphorus pentoxide—while the naphthalene passes on to be frozen out in the U tube placed directly outside of the oven in a trough filled full of cracked ice. The analysis

is complete when the weight of the naphthalene U tube becomes constant or very nearly so at consecutive weighings after a two- or three-hour interval. The volatilization of the naphthalene from the gas is usually complete in six hours. The time required for an analysis of tar varies with the amount of tar in the sample and usually takes thirty or forty hours for standpipe samples when the weight of tar amounts to 8 or 10 grm. When the analysis is complete, the tar volatilizing tube is again weighed, the loss giving the weight of moisture and naphthalene given off. Having the weight of naphthalene in the U tube, we have the weight of moisture also, which, however, is at best only

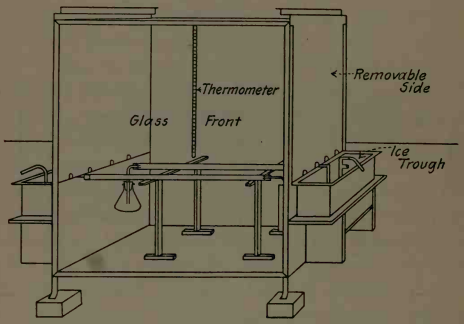

FIG. 38.—Oven for naphthalene determinations.

approximate, because there is always more or less light oil, such as benzene, given off from the tar with the moisture and naphthalene, which cannot easily be estimated. Finally the volatilizing tube is set in a Soxhlet extractor and the remaining contents extracted with chloroform until free of all soluble material. After drying, the tube is weighed, this giving the weight of free carbon in the tar.

The oven used is of galvanized iron and is 20 in. high by 16 in. wide by 14 in. deep. It is shown in Fig. 38 and is arranged so that eight samples may be worked at a time. The drying train consists of a heavy glass tube about 1/2 in. internal diameter and 12 in. long. It contains broken lime for about two-thirds of

its length and phosphorus pentoxide thoroughly incorporated in glass wool for the other one-third. This introduction of the glass wool with the phosphorous pentoxide prevents the gas from forming channels in the latter and thus aids in rendering the extraction of moisture complete before reaching the napthalene U tube. The lime used must be extremely rapid in its reaction with water in order to avoid too great expense for phosphorus pentoxide. It may be readily made by igniting crushed limestone to a dull red heat for two hours in a muffle. If the lumps of lime are too small, the expansion attendant upon their slacking will crack the tube. If the lumps are too large, the gas will not be dried sufficiently. A satisfactory mixture is obtained by taking everything that will pass a four-mesh sieve and will not pass a twelve-mesh. Connection with the naphthalene U tube is made as shown in Fig. 37 at C, through a glass sleeve made air tight by a piece of rubber tubing placed over the whole. This prevents the naphthalene from coming in contact with the rubber. It is well known that rubber absorbs naphthalene. Nevertheless, it has been found safe to use rubber stoppers in the volatilizing oven. Rubber stoppers in frequent use absorb all they can take up and after a few runs cause no further trouble.

This method allows the estimation of napthalene as vapor in the gas, and of water, non-volatile tar, free carbon and napthalene in the suspended tar. The separation of the water and non-volatile tar is not very accurate, the light oils which are vaporized by the air drawn through being reported as water. The estimation of naphthalene is, however, quite accurate. The air passing through will leave the system saturated with naphthalene at the temperature of ice water, but this loss need not amount to over a milligram for each ten hours' run. It is possible that the napthalene may be contaminated by other hydrocarbons and the napthalene deposit is sometimes slightly oily and has a low melting point.

9. Ammonia.—Crude coal gas before scrubbing may contain as much as three-quarters of a per cent. of NH_3 by volume. After the gas has traversed the scrubbers the amount of ammonia should be reduced to a trace. The amount of NH_3 permissible in purified gas in Massachusetts and New York is 10 grains per 100 cu. ft. It is not difficult to conform to this requirement.

The gas to be tested is bubbled through standard acid, suction being produced by an aspirator holding a cubic foot, which also acts as a measuring device. The excess of acid is then titrated back with standard alkali, cochineal being used as an indicator. If the gas contains much suspended tar the end of the titration cannot be observed sharply and it is necessary to make the solution alkaline and redistill the ammonia into standard acid before titrating. One cubic centimenter of $N/_{10}$ acid equals 0.017 grm. NH_3.

10. Cyanogen.—Cyanogen compounds exist in small amounts in unpurified gas. In the purification process they are partly removed in the ammonia scrubbers and largely in the iron-oxide purifiers or in special scrubbers containing compounds of iron. The gas is estimated by bringing it into contact with an alkaline solution carrying suspended ferrous hydroxide and titrating the resultant ferrocyanide. The method according to Mueller[1] is as follows:

"To determine the amount of cyanogen in gas, the cyanogen is converted into potassium ferrocyanide by passing the gas through a caustic potash solution containing freshly precipitated ferrous hydrate in suspension. After filtering, the potassium ferrocyanide is determined in the clear solution by acidifying and titrating with a standard solution of zinc sulphate until all ferrocyanide has been precipitated as zinc ferrocyanide. The end reaction is determined as follows: A drop of a 1 per cent. solution of ferric chloride is put on a piece of white filter-paper absolutely free from iron. A drop of the liquid being tested is then put on the paper near the drop of ferric chloride so that the liquor as it spreads out on the paper will come in contact with the ferric chloride. Care must be taken that the precipitate of zinc ferrocyanide does not come in contact with the iron solution. As long as there is any ferrocyanide left in solution, a blue color will appear where the two drops come in contact due to the formation of prussian blue. When all ferrocyanide has been precipitated this color will no longer appear, which indicates the end point of the titration. The zinc sulphate solution is made by dissolving approximately 5 grm. of pure zinc sulphate in 1 liter of water with the addition of 10 c.c. of sulphuric acid. This solution is standardized with a solution of 10 grm. of potassium ferrocyanide ($K_4Fe(CN)_6 . 3H_2O$) dissolved in water and diluted to 1 liter. Twenty-five cubic centimeters of the potassium ferrocyanide

[1] *Proc. Am. Gas Inst.*, 5, 249 (1910).

solution are put into a beaker and titrated with the zinc sulphate solution, the end reaction being determined as above. One cubic centimeter of the ferrocyanide solution is equivalent to 0.0570 grains of cyanogen, from which the value of the zinc solution is calculated.

"To test for cyanogen in gas put 15 c.c. of a 10 per cent. ferrous sulphate ($FeSO_4 . 7H_2O$) solution into each of three wash-bottles. Add 15 c.c. of 20 per cent. caustic potash solution to each bottle and pass about 3 cu. ft. of gas through these bottles at the rate of about 1 cu. ft. per hour. Rinse the contents of the bottles into a beaker, add 20 c.c. more of the caustic potash solution and heat to boiling. Filter and wash with hot water until a few drops of the filtrate no longer show a blue color when acidified and tested with a drop of 1 per cent. ferric chloride solution. Transfer the filtrate to a 500 c.c. graduated flask, dilute to the mark and shake well. Take 100 c.c. of this solution and transfer to a beaker by means of a pipette. Slowly add dilute sulphuric acid (sp. gr. about 1.5) stirring constantly until the solution becomes slightly acid toward litmus. Then run in the zinc sulphate solution a few drops at a time until the drop test as explained above shows that the ferrocyanide has all been precipitated. From the amount of zinc sulphate solution used the amount of cyanogen in the gas is calculated."

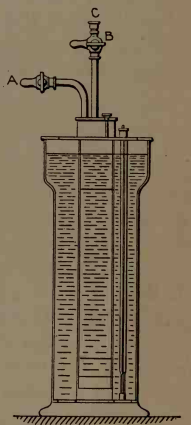

FIG. 39.—Schilling's specific gravity apparatus.

11. Specific Gravity.—The simplest method of determining the specific gravity of gases makes use of the law that different gases streaming through a given orifice at the same temperature and pressure flow through the orifice at a rate inversely proportional to the square root of their specific gravity. Since the time of flow is inversely proportional to the rate, the specific gravity becomes proportional to the square of the time of flow. Bunsen devised an ingenious instrument to measure specific gravities in this way and Schilling later gave it the form which is shown in Fig. 39. It consists of a glass cylinder open at the bottom and fastened to a metal base which keeps it vertical within the larger cylinder of water. It is closed at the top by a metal cap carrying two cocks. A is for the introduction of the gas to be

tested. B is a three-way cock which in one position discharges the gas through a side arm to flush the apparatus. When this cock is in the vertical position the gas passes through a small opening in a platinum plate at C. The apparatus should be standardized against air each time it is used. The calibration is made by opening the air cock and raising the inner cylinder until it is nearly out of water. It will then be filled with air. After closing both cocks it is to be again lowered into the cylinder of water. The observer opens the cock B so that the air streams out through the capillary platinum opening, starts a stop watch as the meniscus passes the lower mark on the gas tube and stops the watch as it passes the upper mark. The instrument is now thoroughly flushed with gas and the time required for the volume of gas between the two calibration marks to stream out of the opening is determined in the same way. The calculation then follows from the formula

$$\frac{\text{sp. gr. gas}}{\text{sp. gr. air}} = \frac{\text{t}^2\,\text{gas}}{\text{t}^2\,\text{air}}$$

12. Natural Gas.—Natural gas is ordinarily distributed and used without any attempt at purification. There is, therefore, much less call for analysis of this product. The most important determination is that of heating value, which is carried out in a gas calorimeter as described for illuminating gas in Chapter VII. If the burner of the calorimeter is adjusted for coal gas it will have to be readjusted for the natural gas and a different tip may have to be inserted. The volume of the natural gas should be controlled to give about the same rise in temperature in the calorimeter as is desirable for coal gas. When a knowledge of the total sulphur is desired it is estimated by the method of § 7 of this chapter. The chemical composition of the gas is characterized by very small amounts of CO_2, O_2 and unsaturated hydrocarbons. The chief constituent is usually methane with variable amounts of ethane and higher homologues. Some gases contain enough gasoline vapors to make it pay to condense them by compression and refrigeration. Burrell[1] reports that the specific gravity of the gas gives good indication of its value for this purpose. Pittsburgh natural gas with a specific gravity of 0.64 when com-

[1] *Bull.* U. S. Bureau of Mines.

pared with air, does not yield commercial quantities of gasoline Gases with specific gravity of 0.95 to 1.60 yield commercially from one to five gallons of 75 to 98° Bé gasoline per thousand cubic feet of gas. Heavy oils of various sorts may also be used as absorbents for gasoline vapors. Since, however, methane is also decidedly soluble in oils the absorptive value of the oil for methane must be previously determined. The United States Geological Survey[1] gives the following as the average composition of natural gas from the three large fields of the United States.

	Average, Pa. and W. Va.	Average, Ohio and Ind.	Average, Kas.
CO_2	0.05	0.20	0.30
H_2S	0.00	0.15	0.00
O_2	trace	0.15	0.00
CO	0.40	0.50	1.00
H_2	0.10	1.50	0.00
CH_4	80.85	93.60	93.65
Other hydrocarbons	14.00	0.30	0.25
N_2	4.60	3.60	4.80

[1] *Mineral Resources of U. S.*, 1909, 2, 297.

CHAPTER XIII

LIQUID FUELS

1. Introduction.—The liquid fuel most frequently used is petroleum in either a crude or semi-refined form. Coal tar and tar products rank next in importance. Alcohol may become important in the future. These fuels, which are to be burned directly, are usually blown into the furnace in a fine spray by means of steam or compressed air. The main points to be determined are their heating value, their behavior in the burner and the relative danger which attends their storage. Fuels which are to be vaporized before combustion, as is the case in internal combustion engines, kerosene lamps, etc., require more elaborate tests which do not come within the scope of this book.

2. Sampling.—The main difficulty in getting a representative sample of liquid fuel is caused by the layer of water and sediment which frequently accumulates on the bottom of a tank of oil or on the surface of one of tar. The main portion of the liquid may also be stratified if various grades have been mixed. The U. S. Bureau of Mines[1] recommends that the oil be sampled as delivered and that either a small stream be run off continuously to a drum from which, after mixing, a smaller sample shall be taken, or that at regular intervals a small dipperful shall be taken from the main stream and placed in a mixing drum. Where it is necessary to sample from a small tank, a proportional sample may be obtained by slowly lowering a glass tube vertically through the oil till the lower end rests on the bottom. If now the upper end be closed by the thumb a column of liquid may be drawn out which represents the composition of the vertical section at the point of sampling. For large tanks the glass tube is replaced by one of tin carrying throughout its length a stiff wire on whose lower end is a tapering cork. When the cork hits the bottom

[1] Technical Paper 3, Bureau of Mines. Specifications for the Purchase of Fuel Oil for the Government twih Directions for Sampling Oil and Natural Gas.

of the tank as the tube is lowered, it is forced up into the tube, sealing the latter so that the sample may be drawn to the surface without leakage. In default of a sampling tube a corked empty bottle with a string tied to the cork may be lashed to a stick and be used. When the bottle has been lowered to the desired depth a pull on the string removes the cork and allows the bottle to fill with oil which can be withdrawn and form part of a composite sample.

3. Heating Value.—The heating value of liquid fuels may be determined in either the bomb or Parr calorimeter in accordance with the general directions in Chapters XVI and XVII. Some difficulty in combustion will be experienced since all the compounds volatilize very rapidly during combustion and there is danger that some of the vapors may break through the flame zone without being completely burned. Incomplete combustion may usually be detected on opening the calorimeter by the odor, and the presence of soot on the inside of the cover. The difficulty becomes greater with volatile liquids like gasoline or alcohol, both because of their greater volatility in the calorimeter and because of the difficulty of weighing the sample accurately.

Slightly volatile liquids such as tar and heavy petroleum oils may be weighed directly into the capsule of the bomb calorimeter and burned completely, if oxygen under 25 atmospheres pressure is used. It is advisable to place on the oil a small weighed pellet of sugar or benzoic acid to start combustion. More volatile liquids must be weighed in thin-walled bulbs of about 0.5 c.c. capacity with capillary necks which the analyst may blow for himself out of fine glass tubing. These are filled by warming the weighed bulb and immersing the open neck in the liquid. Contraction of the air in the bulb draws up a little of the liquid and by repetition of the process the bulb may be filled. The capillary neck may then be sealed close to the bulb with a small blowpipe flame. The increase in weight of the bulb plus the portion of the neck fused off gives the weight of oil in the sample. The sealed bulb is placed on the capsule of the calorimeter and around it is piled about 0.25 grm. of sugar or benzoic acid in contact with the fuse wire. The combustion of this material breaks the bulb and ignites the contents. Richards and Jesse[1] have shown that

[1] *Jour. Am. Chem. Soc.*, 32, 268 (1910).

even this method fails to give complete combustion with volatile liquids like benzene. They recommend the following procedure as successful.

"The benzene in a very thin glass bulb was placed in the bottom of a narrow platinum crucible, 2 cm. in diameter and 2.5 cm. high. A few millimeters above the bulb was fixed a small platform of thin glass bearing a weighed quantity of powdered sugar. The passage of a current through the coil of iron wire ignited the sugar, which in its turn burst the bulb and ignited the benzene at a moment when the whole top of the narrow crucible was filled with flame from the burning sugar. Thus none of the benzene vapor could escape ignition. The trouble with the old method had been that the larger crucible was too wide. Moreover, the sugar had been beneath the benzene instead of above it, so that some of the benzene escaped unconsumed. The amount which thus escaped was greater when there was more nitrogen present than when there was less. Obviously, with non-volatile compounds like sugar the width of the crucible would make no difference."

Gelatine capsules such as used by pharmacists have also been recommended as containers for volatile oils, but their moisture content changes so rapidly in the air that it is difficult to keep constant the necessary correction factor for the gelatine.

The heating value of oils may also be determined in the Parr calorimeter, which is described in Chapter XVII. Non-volatile oils may be weighed directly into the calorimeter which already contains the peroxide mixture, and mixed thoroughly with the charge by means of a stiff wire. Volatile liquids may be placed in the calorimeter in a thin-walled glass bulb as directed for the bomb calorimeter, and the charge of chemicals placed upon it. The calorimeter is then closed with the cap provided and shaken violently until the bulb is broken and the oil is mixed with the peroxide. A correction in addition to those specified in Chapter XVII must be deducted for the heat liberated by reaction between the peroxide and the glass of the bulb. Professor Parr gives this correction as 0.017° C. per 0.1 grm. glass.

The weight of oil taken should be about 0.3 grm. and the charge 10 grm. of Na_2O_2 and 1 grm. of $KClO_3$. The use of 0.2 grm. benzoic acid is also advantageous. Care must be taken that crude petroleum and tars do not carry much emulsified water, for the water reacts with the peroxide with evolution of heat. In ex-

treme cases a violent explosion may take place, wrecking the calorimeter.

If the oil is of such a type that it may be burned without smoke in a burner without a wick and there is at least a pint of the oil available, the most convenient method of determining heat value is in a calorimeter of the Junkers type whose use for determining the heating value of gases is described in Chapter VII. The apparatus as modified for liquids requires a suitable burner for the oil which hangs upon a balance during the determination

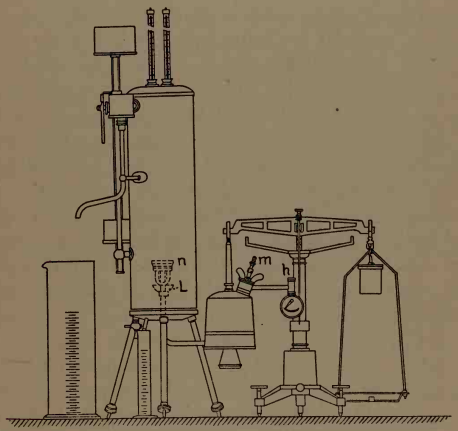

FIG. 40.—Junkers' calorimeter for heating value of oils.

as shown in Fig. 40. The lamp as shown in the illustration requires 150-200 c.c. of oil. To start the lamp the cup L is filled with alcohol which is lighted to preheat the burner head, n. When the alcohol is nearly burned away, air-pressure is placed upon the liquid by a hand pump connected to m. The oil rises in the burner, vaporizes and ignites in the alcohol flame. The pumping is continued until a freely-burning blue flame results when the pump is disconnected. After the water is flowing normally through the calorimeter, the lighted lamp is inserted and centered in the combustion space. When equilibrium has been reached, the balance

is brought to zero by proper adjustment of weights in the pan and the experiment started. After a definite weight of oil, usually 5 or 10 grm., has been burned, the experiment is interrupted and from the rise in temperature and the weight of water heated the heating value of the fuel may be calculated. The details and precautions are in general the same as given for the gas in Chapter VII.

4. Specific Gravity.—The specific gravity of petroleum products is less than 1 and is usually reported on the Baumé scale for liquids lighter than water. Tar is usually heavier than water and its specific gravity is reported directly. If a sufficient quantity of material is available and it is not too viscous, the specific gravity may be determined with approximate accuracy by a hydrometer spindle. If greater accuracy is required or if only a small sample is available a pycnometer or Westphal balance must be used. If a specific gravity on water-free material is demanded, the oil must be put into a flask without the addition of any diluent and distilled slowly till the water is off. The oil distilled is then separated from the water and returned to the residue in the still after it has cooled. A comparison of the Baumé scale for liquids lighter than water and the corresponding specific gravities is given in Table VIII of the Appendix.

5. Moisture.—The various methods for the determination of water in petroleum have been carefully examined by Allen and Jacobs.[1] They recommend a method which involves the measurement of the hydrogen evolved by the action of the water on metallic sodium and also the method of distillation, either with or without the addition of water-saturated toluene or xylene. The latter method will probably give the better results in inexperienced hands. It may be used for tar as well as petroleum products. The toluene is added to diminish the viscosity of the mass and lessen the danger of foaming and bumping. Instead of toluene, xylene or petroleum benzine with a boiling-point of 110 to 150° C. may be used. The diluent must, however, be first shaken with water and then allowed to stand until perfectly clear in order that it may not dissolve any of the water of the sample. The sample of about 100 grm. is weighed into a distilling flask holding at least 500 c.c.

[1] Technical Paper 25, U. S. Bureau of Mines, 1912.

and to it is added a roughly measured volume of 100 c.c. of the diluent or 200 c.c. if the sample is very viscous. The distillation is started slowly and continued until the distillate no longer comes over turbid and approximately as much oil has distilled as was added as a diluent. The distillate is caught in a graduated cylinder and the volume of water read directly after sufficient time has been given for it to settle by gravity. Allen and Jacobs state that the method may be made accurate to approximately 0.033 grm. water for each 100 c.c. of benzene and oil in the distillate.

The details of a similar method for the determination of water in tar as used in the laboratories of the Barret Manufacturing Company have been published by S. R. Church.[1] He specifies exactly the dimensions of the still, the manner of placing the thermometer and other details. The distillation is to be continued until the thermometer in the vapor has reached 205° C. He recommends a convenient form of graduated separatory funnel for the distillate and states that a clean separation of the oil and water can be obtained if 25 c.c. of benzene is introduced into the separatory funnel before the distillation is started.

6. Proximate Analysis.—A proximate analysis in the sense in which it is used in coal analysis is not often made on liquid fuels because they are so largely volatile that the test has little meaning. The ash gives some measure of suspended earthy solids and in the case of tar, the fixed carbon gives an indication of the amount of "free carbon" in the tar. It is necessary to modify the standard method for volatile matter in coal by heating the crucible gently until all foaming has stopped.

7. Suspended Solids.—Suspended solids which in the case of crude petroleums usually are earthy matters and in the case of tars are fine particles of coke forming the so-called "free carbon" are separated by filtration and washing. The oil or tar is first filtered through a 30- or 40-mesh sieve to remove coarse foreign bodies accidentally included. A weighed sample of 5 or 10 grm. is then diluted with pure benzene or toluene until it will filter readily. The solution is filtered through a

[1] *Jour. Ind. and Eng. Chem.*, 3, 228 (1911).

pair of weighed heavy filter papers or through a Gooch funnel and the filter washed with more of the warm solvent until the extraction is complete. The filter is then dried at 105° C. The increase in weight gives suspended solids. If there is much water in the liquid being examined it may be retained on the filter in the form of drops during the first filtration. This water may be driven off by gentle heating and the extraction of soluble material then continued.

8. Flash Point.—The flash point of an oil indicates the temperature at which the oil gives off combustible vapors with sufficient rapidity to form an explosive mixture with the air above it. The flash point will depend upon the rate of heating the oil, the volume of air above it, the rapidity with which the air is replaced and many other variables. It is evident that the conditions must be closely specified in order that results may be of value. Unfortunately there is no standard method as there is for the determination of volatile matter in coal. The figure is of great importance with kerosene oil and most of the states have definite and for the most part different regulations on the subject. The older forms of apparatus were open cups. The more modern forms have closed cups and are best exemplified by the Abel cup and its modifications. This consists of a brass cup 2 in. in diameter set in an air bath which in turn sits in a relatively large water bath to insure even heating of the oil. The oil cup is covered by a brass cover carrying a thermometer and a sliding door. At a touch of a spring the door opens and a small lamp carrying a minute flame is lowered into the air space above the oil. This operation is repeated as the temperature rises until a slight puff which blows the flame out indicates that there has been an explosion. This subject belongs in the domain of the "burning" oils rather than the "fuel" oils and the reader is referred to books on oil analysis for details.

CHAPTER XIV

SAMPLING COAL

1. General Consideration.—However accurate an analysis of coal may be, the results are of little value and are often worse than useless if the sample submitted to the analyst is not a representative one. Elaborate methods have been worked out for sampling gold and silver ores but cost precludes the application of anything but the simplest methods to coal. It is manifest that it is unwise to spend ten cents a ton to determine whether the price is two cents a ton too high. If we assume a shipment of a single car of coal weighing forty tons, which must be sampled and analyzed by itself, it will be seen that the very moderate charge of four dollars for this service will add ten cents per ton to the price of coal. This is probably 10 per cent. of the cost of the coal at the mouth of the mine and is an expense which is hardly justifiable.

However if the test is worth making at all it must be on a sample which has fair claim to representativeness. The coal sampler stands eternally between the devil of inadequateness and the deep sea of excessive cost. In a few large plants where the coal is immediately crushed and removed to storage bins by conveyors a representative sample may readily be obtained. In most cases, however, the coal must be sampled as it comes from the car and the problem is more difficult.

To many people coal is black and all that is black is coal. The more careful observer may detect bits of slate, and streaks or nodules of the brassy looking pyrites. The chemist knows that in addition the fine particles which have crushed because of their greater friability differ in composition from the lump coal and are usually higher in ash, though sometimes the reverse is the case, and that coal is far from being a mass of uniform composition.

Difference in Composition of Lump and Fine Coal

The following tests taken from the author's record of cooperative tests undertaken jointly by the University of Michigan Gas Experiment Station and the United States Bureau of Mines to determine the availability of various coals for gas manufacture show some interesting variations. The coals had mostly been shipped in a small lots in sacks and were therefore considerably crushed in transit. They were screened in lots of about 600 lb. on a 3/4-in. bar screen preparatory to gas tests and the screenings and lump coal separately sampled.

The sampling of the fine coal presented no difficulty since it was already in small lumps and could be crushed as fine as desired. The lump coal could not be finely crushed without detriment to the gas tests and so it was sampled by breaking the large lumps and then taking about two scoopfuls which were crushed and sampled as usual. Of the eleven coals tested in this manner four, one each from West Virginia, Colorado, New Mexico and Wyoming showed very little difference between the lumps and screenings. One coal showed decidedly less ash in the screenings than in the lump coal. Six coals showed noticeable and in some cases notable increases of ash and sulphur in screenings with corresponding decreases of heating value, as shown by the following analyses of the coals calculated to a dry basis.

In the coal from Hellier, Kentucky for which there are three tests, the average heating value of the screenings is 1080 B.t.u. lower than that of the lump. This is entirely due to difference in ash as shown by the figures for heating value figured to coal dry and free from ash, where the difference disappears, the average heating value of the screenings being only 6 B.t.u. below that of the lump. The same thing is true of the other coals of the list—the variation in heating value of lump and screenings disappears almost completely when calculated to a moisture and ash-free basis.

Sulphur is never lower in the screenings than in the lump and is in some cases nearly twice as high.

The last coal in the above table differs from all the others in that the screenings are much lower in ash than the lump. It might be thought that the sample had been labelled incorrectly

COMPARISON OF COMPOSITION AND HEATING VALUE OF LUMP COAL SCREENED OVER A 3/4-IN. BAR SCREEN AND THE SCREENINGS

Coal from	Test No.	Per cent. screenings	Dry coal						Coal dry and free from ash B.t.u.	
			Per cent. ash		Per cent. sulphur		B.t.u.			
			Lump	Screenings	Lump	Screenings	Lump	Screenings	Lump	Screenings
Allegheny Co., Pa.	32	17.4	5.00	8.44	0.87	1.36	14,386	13,948	15,142	15,234
Hellier, Ky.....	21	30.8	6.41	13.24	0.44	0.48	14,234	13,144	15,210	15,149
Hellier, Ky.....	30	48.5	3.88	8.22	0.46	0.57	14,665	13,615	15,257	15,194
Hellier, Ky.....	54	33.0	3.32	9.91	0.61	0.66	14,820	13,712	15,220	15,328
Blocton, Ala.....	33	23.4	4.41	14.91	0.51	0.67	14,380	12,634	15,043	14,848
Saginaw, Mich...	34	9.7	5.90	8.40	1.08	1.83	13,730	13,369	14,591	14,594
LaFollette, Tenn..	31	8.4	2.24	5.38	0.74	1.25	14,706	14,207	15,039	15,016
Harrisburg, Ill....	35	27.9	7.54	9.92	2.06	2.68	13,550	13,235	14,656	14,693
Harrisburg, Ill....	46–7–8	26.6	6.80	10.86	1.80	3.04	13,676	12,940	14,675	14,517
Oak Creek, Colo..	24	39.5	15.67	6.97	1.08	1.63	11,799	13,165	13,991	14,152

of it were not for the check afforded by analysis of the coke made from the lump coal. The coke contained 25.3 per cent. of ash, a figure which agrees well with the calculated result of 24.3 per cent. It is evident that in this coal the coal substance is the friable constituent while the ash forms a cementing material. The heating value of the dry screenings is 1366 B.t.u. higher than the lump, but when the ash is eliminated by calculation, the difference drops to 61 B.t.u.

These figures show that the heating value of lump coal may vary as much as 2000 B.t.u. from that of fine coal and that usually the fine coal will contain more ash and have the lower heat value. Occasionally the reverse is the case. The true coal as reckoned to a moisture and ash free basis has practically the same heating value irrespective of its physical fineness.

2. A Scoopful as a Sample.—It is commonly held that a few scoopfuls should be representative of a carload. This question was put to a practical test by Bailey[1] who had a lot of 3 tons of run-of-mine coal carted away in wheel barrows. As each barrow was filled a shovelful of coal was put into, not one, but into each of sixteen sample barrels. After the pile had disappeared there were left the sixteen sample barrels each with about 125 lb. of coal. These samples were crushed and sampled carefully and the ash in each was determined. The results were as follows:

	Per cent. ash	
1	9.68	
2	10.28	
3	13.92	Maximum
4	11.22	
5	10.88	
6	9.80	
7	11.84	
8	10.28	
9	10.10	
10	10.64	
11	10.06	
12	10.72	
13	9.46	Minimum
14	9.66	
15	11.08	
16	11.34	

[1] *Trans. Am. Soc. Mech. Eng.*, 27, 639 (1906).

These samples which should have given results in close agreement show an extreme variation of 4.46 per cent. in their ash content. Had the heating values of these samples been determined they would of course have shown similar discrepancies. If this coal has been sold on a premium and penalty basis and the coal with the average ash content of 10.68 would have been accepted without premium or penalty, the penalty on a basis of sample No. 3 might readily have been six or eight cents per ton. And yet in this test the sample consisted of four or five shovelfuls taken from a lot as small as 3 tons and not from a whole car load.

3. Influence of Lumps of Slate.—It is manifest that if all the ash of coal were to be concentrated in lumps the size of a football, that a single scoopful of coal would either show no ash or else an exorbitantly high amount. The error would be much less if the ash were in lumps only the size of walnuts and still less if it were more finely divided. Even if the ash were in large pieces if a sufficient number of scoops should be taken for analysis an average of all the figures would give a correct result. Bailey[1] gives the following table derived partly experimentally and partly mathematically showing the relation between the size of the largest piece of slate and the weight of the sample which must be taken in order that error in sampling shall not cause an error of over 1 per cent. in the ash.

Size of slate, inches	Wt. largest piece of slate, pounds	Original sample should weigh, pounds
4	6.7	39,000
3	2.5	12,500
2	0.75	3,800
1	0.12	600
0.75	0.046	230
0.50	0.018	90

Since there are very few shipments of coal other than the small sizes of anthracite which may not contain pieces of slate weighing a pound it is evident that on this basis a sample of less than 2 tons cannot be considered representative. Any smaller sample whether it be drawn from a wagon load or a

[1] *Jour. Ind. and Eng. Chem.*, 1, 176 (1909).

train of cars cannot be considered as representative of anything except itself.

4. Taking a Sample.—It is fatal for a sampler to try and pick an average sample by taking what seems to him a fair proportion of coarse and fine, and rejecting material that looks either exceptionally good or bad. The only way is to determine how a most representative sample may be secured in a reasonable manner and then to carry out the operation as mechanically as possible.

If the sample is being taken from a wagon the shovel should be run along the bottom of the wagon after enough has been unloaded to allow the coal to assume its natural slope. The same procedure may be followed when coal is being shovelled from flat-bottomed cars. Where cars or wagons are being dumped the scoop may be held in the stream of falling coal. If cars are to be sampled before unloading, a trench, or better two trenches, each 12 in. deep should be dug across the car in order to remove excess of dust and cinder as well as snow which may have collected in the top layers. The sample is to be taken from the bottom of the trench. It is evident that coal sampled in this way will contain too small a proportion of fine coal, most of which will have sifted to the floor of the car. It is therefore preferable to sample during unloading.

If it is necessary to determine the moisture in a car of coal which arrives wet or covered with ice the problem of sampling becomes even more complex. Fortunately, specifications are usually based on dry or air-dry coal so that the accidental moisture acquired in transit is not usually of importance.

5. Mine Sampling.—The methods of sampling coal in a mine as recommended by the U. S. Bureau of Mines have been fully described by Holmes.[1] He recommends that for mines shipping 200 tons or less daily, at least four samples should be taken. In general only clean, fresh coal should be taken and weathered coal should be avoided. Before cutting a sample the face of the bed and the roof is to be cleaned of loose fragments which might drop into the sample and a band 1 ft. wide extending from floor to roof is to be cut back at least an inch to expose fresh coal. The sample as cut from this prepared face should

[1] Technical Paper 1, Bureau of Mines, 1911.

include everything which the miner includes in the coal prepared for the market and should exclude the thick partings and large lenses of pyrite which are thrown out by the miner. The cut should be made perpendicularly about 2 in. deep and 6 in. wide so that there will be about 6 lb. of coal chips for each foot of thickness of the vein. These chips are to be caught on the waterproof sample blanket and crushed to pass a 1/2-in. screen. The sample is then quartered down and placed in a tight sample can. All the operations are to be carried on in the mine so as not to expose the coal to the outside atmosphere.

6. Preparation of Sample.—The initial sample must be crushed and subdivided until it is finally ready for the chemical analysis. Care must be taken that it does not change during this process. It is almost impossible to prevent the moisture from changing and where it is necessary to determine this, the whole sample is usually weighed and allowed to dry in a warm room until it has become approximately air-dry, when it is again weighed. It is in any case difficult to sample coal which is very wet or covered with ice and a preliminary air-drying is, where possible, alway advisable. The sample must now be crushed and subdivided. Bailey, in the reference already cited, gives the following rules for subdivision:

Weight of sample to be divided, pounds	Should be broken to inches
7500	2
3800	1.5
1200	1
460	0.75
180	0.5
40	2 mesh
5	4 mesh
0.5	8 mesh
0.25	10 mesh

Where a well-equipped sampling laboratory is available the crushing will of course be easily accomplished by crushers and the subdivisions either made by mechanical samplers or upon clean iron plates. In such cases there is very little liability to error in this stage of the process. In many cases,

however, the crushing and subdivisions must be carried out by hand, often on the floor of the boiler room and frequently under even less favorable conditions. The first requisite is cleanliness of the sampling surface. It is always preferable to sample on a metal plate. A cement floor is to be looked upon with suspicion and not to be used unless it is hard and fails to yield appreciable sand on vigorous sweeping. The liability to error is not great while the sample is large. When it becomes small enough it should be placed on oil cloth if a metal plate is not available.

When working with a large sample the lumps may be crushed by a hammer or stamp to the size indicated and the material shovelled up, one shovelful out of every four going to the sampling barrow. All the coal should be shovelled away in this manner and the floor swept clean. It is not sufficient to shovel into the sampling barrow approximately one-fourth of the sample pile and leave the other three-fourths behind, for this process might include in the sample all the fine pieces resulting from one large piece of slate. When the sample has been reduced to 400 or 500 lb. it is customary after crushing to shovel the coal into a cone which is shovelled out again into a ring, care being taken to distribute the coal on the ring with a circular motion in order to distribute the fine pieces resulting from one large piece of slate. This ring is again to be shovelled into a cone, the sampler going round and round the ring and placing each shovelful of coal on the apex of the cone so that it may run down as nearly evenly as possible around the circumference. The dust which cannot be shovelled up is then swept radially to the cone, the cone is flattened and cut into quarters by the shovel. The whole of one quarter including the sweepings is then shovelled into a tight barrow or bucket, the sampling floor is cleared and the process repeated until the sample is sufficiently reduced. The final sample should weigh 4 or 5 lb. and be crushed to 1/8-in. size. It should at once be placed in a tight bottle or can and plainly labelled.

7. Preservation of Sample.—If the percentage of moisture in the coal is of importance the sample should be placed in an air-tight receptacle and kept in a cool place. Coal which is not finely powdered does not change rapidly but it is advisable

to have the analysis made promptly. Porter and Ovitz[1] have shown that samples of coal evolve methane and carbon dioxide and absorb oxygen for a period of several months. The changes due to the evolution of methane seldom rise above one-tenth of 1 per cent. The changes due to addition of oxygen are less certain but would seem to be possibly as high as 1/2 per cent. Parr has shown that Illinois coals may lose in heat value from 1/2 to 1 per cent. in the first ten days after mining and during the process of preparing the sample for analysis. The rapid changes take place soon after the coal is mined and the rate of change has usually materially decreased before the coal is sampled by the consumer.

8. Usual Accuracy of Sampling.—The figures given by Bailey show that an accuracy of 1 per cent. in the ash is not to be expected by ordinary methods. The following tables give some data resulting from the sampling of two separate carloads of coal. Four separate samples were taken from each car after loading at the mine by an inspector of the Bureau of Mines. The cars on arrival were sampled especially carefully, one-sixth of each carload being systematically separated as it was unloaded for the initial sample. This initial sample was cut into four separate ones which were separately sampled and analyzed. There are eight different samples from each carload whose analyses are tabulated in the accompanying table.

PITTSBURG COAL, A. A. 15

		Air-dried coal				B.t.u. of coal free from moisture and ash
		Moisture	Ash	S	B.t.u.	
Car at mine	No. 1...	0.95	6.27	0.91	14213	15319
	No. 2...	1.00	5.55	0.72	14315	15318
	No. 3...	0.98	6.23	0.98	14182	15284
	No. 4...	0.96	6.91	0.84	14107	15295
	Average	0.97	6.24	0.86	14204	15304
Car as unloaded	No. 1...	1.11	5.99	0.82	14215	15301
	No. 2...	0.97	6.54	0.93	14137	15284
	No. 3...	1.01	5.63	0.80	14285	15300
	No. 4...	1.08	5.88	0.81	14206	15269
	Average	1.04	6.00	0.84	14211	15288

[1] Technical Paper 2, Bureau of Mines, 1911.

FAIRMONT COAL, A. A. 16

		Air-dried coal				B.t.u. of coal free from moisture and ash
		Moisture	Ash	S	B.t.u.	
Car at mine	No. 1...	1.10	7.62	0.67	13925	15255
	No. 2...	1.10	7.71	0.64	13874	15216
	No. 3...	1.07	9.23	0.83	13678	15240
	No. 4...	1.17	6.20	0.52	14096	15217
	Average	1.11	7.69	0.66	13898	15232
Car as unloaded	No. 1...	1.24	8.87	0.64	13671	15209
	No. 2...	1.21	8.98	0.69	13640	15188
	No. 3...	1.28	8.89	0.69	13638	15182
	No. 4...	1.27	9.06	0.73	13604	15160
	Average	1.24	8.95	0.69	13638	15185

The chief variable in these samples is the ash which in turn affects the heating value. The accuracy of the analyses is attested by the close agreement of the heating value referred to coal dry and free from ash. In the Fairmont coal the heating value of the coal taken at the mine is noticeably higher than that sampled from the car, when calculated to an ash and moisture free basis, due possibly to escape of gas from the freshly mined coal.

The average ash content of the Pittsburgh coal is closely the same in the two sets but in the Fairmont coal the average ash as sampled from the car at the mine was 1.6 per cent. lower than that obtained as the car was unloaded. As was pointed out above, this variation is a normal one due to the method of sampling. The variation in the average heating value of these two series amounts to 260 B.t.u., a figure which might easily cause a difference in price of five cents a ton.

Turning from averages to individual figures we find a better agreement with the Pittsburgh than the Fairmont coal, and in each series the agreement better between the samples taken from the car as unloaded, as should have been the case. The extremes for the Fairmont coal are tabulated as follows:

	Low ash		High ash		Difference	
	per cent. ash	B.t.u.	per cent. ash	B.t.u.	per cent. ash	B.t.u.
Car at mine.....	6.20	14096	9.23	13678	3.03	418
Car as unloaded .	8.87	13671	9.06	13604	0.19	69

The agreement between the samples taken very carefully

from the car as unloaded is excellent. The difference between the extremes of the samples taken from the loaded car which amounts to 426 B.t.u. might readily cause a difference of nine cents a ton on the settlement price of the coal.

The engineers of the U. S. Bureau of Mines[1] have studied the error in sampling on ten different lots of coal. Each of two inspectors collected a sample of 100 lb. from a given lot of coal. In lot *a* their samples differed in heating value by 158 B.t.u. per pound of dry coal. They then each collected a second sample of 100 lb. and averaged the results of this with their first sample. The difference between the two collectors than dropped to 132 B.t.u. In the same way they continued to take successive samples of 100 lb. and average all of their results and after ten of such samples had been taken the differences between the averages for each man was small. As the result of tests on ten different lots of coal they found that it was necessary to collect and average seven different samples of 100 lb. each in order that the results obtained by two collectors should not differ by more than 50 B.t.u. Their average results are given in the following table.

AVERAGE ERROR IN SAMPLING 10 LOTS OF COAL AS SHOWN BY THE DISAGREEMENT IN HEATING VALUE OF SUCCESSIVE SAMPLES TAKEN BY TWO COLLECTORS

	Disagreement between two collectors in B.t.u. per pound dry coal
First sample of 100 lb.	251
Average of 2 samples of 100 lb.	200
Average of 3 samples of 100 lb.	125
Average of 4 samples of 100 lb.	111
Average of 5 samples of 100 lb.	75
Average of 6 samples of 100 lb.	78
Average of 7 samples of 100 lb.	51
Average of 8 samples of 100 lb.	53
Average of 9 samples of 100 lb.	44
Average of 10 samples of 100 lb.	37
Average of 11 samples of 100 lb.	32
Average of 12 samples of 100 lb.	32
Average of 13 samples of 100 lb.	25

The Bureau of Mines recommends that the gross sample collected

[1] *Bul.* 63, Bureau of Mines.

be never less than 1000 lb. In sampling cargo deliveries of 5000 and more tons the recommendation is that the sample be from 4000 to 5000 lb. and that the sample be crushed in approximately 500-lb. lots from each of which a sample is sent to the laboratory. Four or five analyses are usually made for each cargo and the results are averaged. Detailed directions for sampling and also specifications for coal as used by the Government are given in *Bulletin* 63 of the Bureau of Mines entitled Sampling Coal Deliveries and Types of Government Specifications for the Purchase of Coal by George S. Pope. Copies may be obtained from the Director of the Bureau of Mines in Washington.

9. Reliability of Samples.—It is evident from the preceding paragraphs that it is possible to sample crushed coal with fair accuracy, but that it is not possible to accurately sample coal containing large lumps without greater expense than is usually warranted. The error is largely an accidental one due to the inclusion or rejection of too many or too few of the larger pieces of slate in the sample. There may also be a systematic error if care has not been taken to get a proper proportion of coarse and fine coal. So far as the error is accidental, it will diminish, according to the law of probabilities, with increasing number of samples, so that although any one sample may be in error by 3 per cent., the average of fifty samples should be quite accurate. Contracts which involve the delivery of coal throughout the year may therefore be equitably settled on a sliding scale based on analysis, for the undue premium on one shipment will be counterbalanced by the undue penalty on another and in the course of a year a fair average will have been reached. If it is necessary to determine accurately the value of a single shipment, greater care and expense is necessary than the sum at issue will usually warrant.

CHAPTER XV

THE CHEMICAL ANALYSIS OF COAL

1. Introduction.—The methods used in analysis of coal may be grouped into two main divisions. In *ultimate analysis* the aim is to report as accurately as may be the percentages of the chemical elements, especially carbon, hydrogen, nitrogen, oxygen and sulphur. These elements are reported as elements without any attempt to indicate the manner in which they are combined in the coal. This method of analysis is scientifically valuable but finds few applications in technical work. In *proximate analysis*, on the other hand, the attempt is made to group the constituents of the coal according to certain physical properties which are technically important such as moisture, volatile matter and ash. This method of analysis is of great commercial importance. These two methods of analysis are applicable to all forms of solid and liquid fuel—peat, lignite, bituminous coal, anthracite, coke, petroleum, tar, etc.—with slight modifications required by the physical properties of the fuel being investigated.

2. Proximate Analysis.—The usual items included in a proximate analysis are moisture, volatile matter, fixed carbon and ash. Sulphur is frequently included in the report, but is determined separately. There is no difficulty in comprehending what is meant by the terms moisture and ash. The expressions volatile matter and fixed carbon require explanation, for they are merely relative terms which can be interpreted only by reference to certain definite conditions of analysis. If coal be heated to redness the heat will decompose a portion of the coal substance. Part of this decomposed coal will be evolved as a thick black smoke which will burn in the air and part will remain behind as a solid coke or carbonaceous reside. If tar or petroleum be treated in this manner part of the substance will be driven off in the same form in which it existed in the oil. In the case of coal the material volatilized is formed only through the decomposing action of the heat. In proximate

analysis no attempt is made to separate these two classes of products. Everything which is evolved in the process is called "volatile." The residue remaining in the crucible after this process consists of ash and a material which is largely carbon and which forms the so-called "fixed carbon." The percentages reported as volatile matter and fixed carbon will vary with every modification of the conditions of analysis. The moisture and ash are also liable to vary with change in detail of method. It is therefore very important that all chemists use the same method in order that their results may be comparable. In 1899[1] a committee of the American Chemical Society which had made a careful study of the subject reported a scheme of analysis which has been generally recognized as standard for the United States. In 1910 a joint committee of the American Chemical Society and the American Society for Testing Materials was formed to consider a revision of these methods, and their suggestions as embodied in their preliminary report[2] are included in this chapter.

3. Preliminary Examination of Sample.—In the preceding chapter on Sampling the precautions to be observed in taking the initial sample and in subdividing it were discussed. There is no definite point where the sampler is to stop in his process of subdivision and turn the material over to the chemist, but since the sampler is in general a field worker it is customary to consider his work as ended when the sample has been reduced in weight sufficiently to allow its easy transportation to the laboratory. Sometimes it is stated that the sample sent to the laboratory should weigh from 3 to 5 lb.

The chemist receiving a sample should note the nature of the package as well as its marks. Coal shipped in a canvas sack or a paper carton which is not tight will almost certainly have changed in moisture content and will probably have lost some of its finer particles. After opening the package the net weight of sample and an at least approximate estimate of its physical condition should be recorded. Information as to whether the sample as received was wet or dry and whether it showed evident pieces of slate or pyrite is sometimes of importance. The size of the

[1] *Jour. Am. Chem. Soc.*, 21, 1116 (1899).
[2] *Jour. Ind. and Eng. Chem.*, 5, 517 (1913).

largest lumps relative to the size of the sample shipped will give some indication of the care which has been used in the preparation of the sample. The chemist should, for his own protection, state in his report when the sample is manifestly a non-representative one, and when insufficient care has been exercised in packing it for shipment.

The 1913 report of the Committee on Coal Analysis recommends that the size of sample to be transmitted to the laboratory vary with the size of the coal as follows:

Size of largest impurities	Minimum weight of sample
1/2 in.	75 lb.
3/8 in.	30 lb.
1/4 in.	9 lb.
3/16 to 1/5 in. = 4 mesh	5 lb.
1/8 in.	3 to 5 lb.

4. Air-drying.—It is inconvenient to handle samples of coal which are wet, since they clog the mills and cannot be mixed readily. They also change in weight rapidly in the air. It is therefore standard practice to air-dry the sample. This may be accomplished by spreading in a thin layer in a tin pan placed in a warm room for twenty-four hours or longer if necessary to bring it to approximately constant weight. The process may be hastened by placing the samples in an oven such as is used at the Bureau of Mines[1] which is heated to not over 100° F. and wh ch is provided with forced ventilation. In this oven, which is illustrated in Fig. 41, air is heated by a Bunsen burner and circulated by a small electric fan. The loss in weight during this process is reported as air-drying loss. All analyses are made on this air-dried coal since it may be weighed and handled in the air with relatively slight change of weight. There is evidence that the coal slowly changes in this air-drying process, so that it should not be exposed to the air longer than necessary. Porter[2] reports that Pittsburg coal on drying eight days at 35° C. absorbed 0.17 per cent. of oxygen and that a Wyoming coal similarly treated absorbed 0.70 per cent.

[1] *Technical Paper* 8, *Bureau of Mines*, 1912.
[2] *Jour. Ind. and Eng. Chem.*, 5, 520 (1913).

5. Grinding and Preserving the Sample for Analysis.—The sample of coal which has been air-dried or is at least so nearly air-dry that it does not change in weight in the air rapidly is to be crushed and subdivided until a portion of 50 or 60 grm. is obtained from which a sample of 1 grm. may be taken which

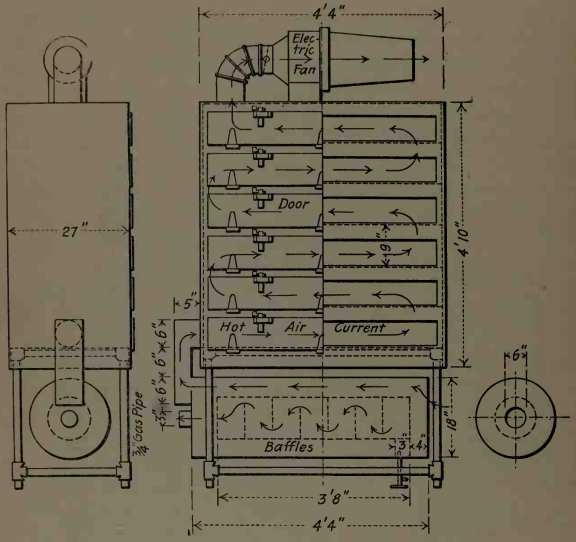

FIG. 41.—Oven for air-drying coal samples.

shall be representative of the whole original mass of coal. Bailey in the reference quoted in the preceding chapter gives the following rules for subdivision in the laboratory.

Size of coal mesh	Should not be divided to less than
2	8300 grm.
4	1100 grm.
8	120 grm.
10	55 grm.
20	3 grm.

He recommends that as soon as the sample has been put through an 8-mesh sieve that it be all crushed to 60-mesh or finer.

The crushing to 12-mesh may be done by hand in a mortar or in any type of crusher without much danger of injuring the sample if it is done rapidly. It is necessary to take precautions, however, to prevent injury to the sample during fine grinding, for finely ground coal absorbs oxygen from the air rapidly and gives off water. The exact nature of this reaction is not understood but it is known to sensibly affect the heating value. This change is accelerated if the sample becomes heated during the fine grinding. For this reason disc grinders should be used with great caution. They grind rapidly but the plates get hot, sometimes hot enough to start destructive distillation of the coal, which manifests itself by a tarry odor. If the disc grinder is used the plates must not be set closer than necessary and the coal must be fed very slowly. The best method of finely grinding coal is to use a jar mill. This consists of a heavy porcelain jar provided with a cover which may be clamped tight on a rubber gasket. It is filled about one-third full of round flint pebbles or porcelain balls and is placed in a frame where it may be rotated at the rate of 50 to 75 revolutions per minute. The balls tumbling over each other fall with sufficient force to crack the small pieces of coal, but are themselves worn off to only a negligible extent. The longer the coal is left in the jar the finer it becomes and it is easy to get any desired degree of fineness. The size of the jar required and the diameter of the pebbles will vary with the hardness of the material and the size of the lumps. If the lumps have a diameter even as great as one-fourth that of the pebbles, some of the lumps may become simply rounded balls themselves and not be crushed by the impact of the pebbles. If the coal has been put through a 10- or 12-mesh sieve before going into the ball mill a jar of 8 in. internal diameter and with pebbles 3/4 in. or 1 in. in diameter will grind the sample properly, provided the coal does not occupy over one-sixth of the volume of the jar. When the grinding is completed the jar is emptied onto a coarse sieve which retains the balls. The coal should be tested on a 60-mesh sieve and any portions failing to pass it should be separately ground to pass an 80-mesh sieve and added to the main portion. These coarse particles

are liable to be slate or pyrites and therefore especial care must be taken to see that they are finely ground and mixed with the main sample. A coal ground to pass a 60-mesh sieve is fine enough to make a 1-grm. sample as representative of the lot as the various intermediate samples were of the initial sample. It is not desirable to grind the coal much finer because of the increased error due to loss of moisture and absorption of oxygen by the finely powdered coal.

This finely ground sample may now be stored as a whole in a fruit jar or subdivided and an amount of only 50 grm. placed in a wide-mouthed bottle closed with a rubber stopper. The bottle should be filled only half full so that the analyst before weighing out his sample may gently shake and rotate the bottle to mix the contents. Pyrites and slate tend to work to the bottom of a sample bottle and the precaution of mixing before taking a sample should never be omitted.

Even the most carefully preserved coals deteriorate in time. Parr[1] has shown that in three years' storage in the laboratory Eastern coals lose in heating value to the extent of 0.5 to 1.5 per cent., while Illinois coals deteriorate to the extent of 3 to 5 per cent. Coals which are to be kept for a long period should be sealed as nearly air-tight as possible.

6. Moisture.—The determination of moisture in coals is complicated by the change which the coal substance itself undergoes when subjected to heat and exposure to the air. The method recommended by the committee of the American Chemical Society in 1899 prescribes that 1 grm. of the coal shall be dried in an open porcelain or platinum crucible at 104-107° C. for one hour and shall then be cooled in a desiccator and weighed covered.

The errors in the determination of moisture in coal have been studied by several investigators, among them Hillebrand and Badger[2] at the Bureau of Standards. They conclude that the most nearly correct results may be obtained by drying *in vacuo* over concentrated sulphuric acid for a period of two days or more. The method prescribed above of heating for one hour in a closed oven at 105°–110° C. showed the moisture to be

[1] Eighth Internat. Congr. Appl. Chem., 10, 225 (1912).
[2] Eighth Internat. Congr. Appl. Chem., 10, 187. (1912).

roughly nine-tenths as great as that obtained by the vacuum method when the comparisons were made on coals which had not been unduly weathered. If the heating in the oven was prolonged an hour longer the apparent moisture rose somewhat, but was still below that obtained by the vacuum method. If the coal was heated for one hour in an oven through which dry air was circulated, the results obtained were much more consistent and in most cases approached quite closely those obtained in a vacuum.

The method adopted as standard by the U. S. Bureau of Mines, as given in their Technical Paper 8, is to take a 1-grm. sample of the 60-mesh coal, place it in a weighed 7/8 in. by 1 3/4 in. porcelain crucible and heat for an hour at 105° C. in a constant temperature oven in a stream of dry air. The crucible is then removed from the oven, covered and cooled in a desiccator over sulphuric acid. The loss in weight multiplied by 100 is counted as the percentage of moisture. The oven which they use is of copper with double walls. The space between the inner and outer wall is filled with a solution of approximately 45 parts by weight of glycerine and 55 of water, the exact proportions being modified to get a solution boiling at 105° C. A reflux condenser prevents change in boiling-point through evaporation of the water. A current of air dried by passing through sulphuric acid and preheated by passing through a copper spiral immersed in the glycerine is forced into the drying chamber at the back and escapes through a small hole in the door. The air is blown in at a rate sufficient to change the volume of air in the oven from 8 to 10 times an hour.

The 1913 report of the Committee on Coal Analysis recommends that the sample of approximately 1 grm. be weighed into a pair of shallow weighing capsules with ground caps. For anthracite and bituminous coals the capsules are to be placed open in a preheated oven at 104-110° C., through which passes a current of air dried by concentrated sulphuric acid. After being heated for one hour in this oven the capsules are to be removed, covered at once and cooled in a desiccator containing concentrated sulphuric acid. Sub-bituminous and lignitic coals are to be dried in a stream of dry carbon dioxide or nitrogen. After the samples are dried they are to be placed in a

vacuum desiccator which is then exhausted to remove absorbed carbon dioxide. After exhaustion the desiccator is refilled with dry air.

7. Volatile Matter.—There can never be an absolute method for the determination of volatile matter, for only a very small proportion of the material evolved from coal at a red heat was present as such in the coal. Most of this volatile material is a decomposition product whose amount varies with the rate of heating, the maximum temperature attained, the character of the flame, the size of the crucible and other conditions. It is necessary, therefore, in a standard method to fix every possible variable as rigidly as possible.

The 1899 method of the American Chemical Society is as follows:

"Place 1 grm. of fresh, undried, powdered coal in a platinum crucible, weighing 20 or 30 grm. and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom six to eight centimeters above the top of the burner. The flame should be fully twenty centimeters high when burning free, and the determination should be made in a place free from draughts. The upper surface should remain covered with carbon. To find 'Volatile Combustible Matter' substract the per cent. of moisture from the loss found here."

More recent investigations especially by Fieldner and Davis[1] and by Parr[2] have thrown some light on the causes of variation. The former authors working in the laboratories of the U. S. Bureau of Mines at Pittsburgh and Washington found that the carburetted water gas of Washington gave a maximum temperature of 970° C. within the crucible which was 120° hotter than could be obtained with the coal gas of Pittsburgh or with natural gas burned under favorable conditions. They summarize the results of their experiments as follows:

"Two laboratories are likely to vary 2 per cent. in volatile matter, both using the official method (of 1899). The percentage of volatile matter obtained from the same sample of coal varies with the temperature and rate of heating. This is not sufficiently defined by height

[1] *Jour. Ind. and Eng. Chem.*, 2, 304 (1910).
[2] *Jour. Ind. and Eng. Chem.*, 3, 900 (1911).

of flame. Temperatures ranging from 760° C. to 890° C. may be attained with a 20-cm. natural gas flame, when the gas pressure is varied from 1 to 13 in. of water; variations of 2 per cent. volatile matter are thus produced. Differences in type and sizes of burner influence results from 0.3 to 1.5 per cent. Polished crucibles become hotter and yield about 1 per cent. more volatile matter than dull gray ones. Laboratories using natural gas are apt to get results on volatile matter that are considerably lower than those using coal gas, unless the following precautions are observed: (1) Gas should be supplied to the burner at a pressure of not less than 10 in. of water. (2) Natural gas burners admitting an ample supply of air should be used. (3) Gas and air should be regulated so that a flame with a short, well-defined inner cone is produced. (4) The crucibles should be supported on platinum triangles and kept in well-polished condition."

The 1913 report of the Committee on Coal Analysis recommends the following two alternate methods for the determination of volatile matter.

"It is recommended that for volatile matter determinations a 10-grm. platinum crucible be used having a capsule cover, that is, one which fits inside of the crucible and not on top. The crucible with 1 grm. of coal is placed in a muffle maintained at approximately 950° C. for seven minutes. With a muffle of the horizontal type, the crucible should not rest on the floor of the muffle but should be supported on a platinum or nichrome triangle bent into a tripod form. After the more rapid discharge of the volatile matter, well shown by the disappearance of the luminous flame, the cover should be tapped lightly to more perfectly seal the cover and thus guard against the admission of air.

"One gram of coal is placed in a platinum crucible of approximately 20 c.c. capacity (35 mm. in diameter at the top and 35 mm. high). The crucible should have a capsule cover which will readily adjust itself to the inside upper surface of the crucible. The crucible is placed in the flame of a Meker burner, size No. 4, having approximately an outside diameter at the top of 25 mm. and giving a flame not less than 15 cm. high. The temperature should be from 900° to 950° C. determined by placing a thermocouple through the perforated cover which for this purpose may be of nickel. The junction of the couple should be placed in contact with the center of the bottom of the crucible. Or the temperature may be indicated by the fusion of pure potassium chromate in the covered crucible (fusion of K_2CrO_4, 940° C.). The crucible is placed in the flame about 1 cm. above the top of the burner and the heating is continued for seven minutes. After the main part

of the gases have been discharged the cover should be tapped into place as above described.

"For lignites a preliminary heating of five minutes is carried out, during which time the flame of the burner is played upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating the crucible is placed in the full burner flame for seven minutes as above described."

8. Ash.—The ash of coal is generally defined as the mineral residue remaining after complete combustion. The 1899 method of the American Chemical Society is as follows:

"Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol."

The errors attending the determination of ash have been studied very carefully by Parr[1], who has shown that 90 per cent. of the Illinois coals carry as much as 0.2 per cent. of calcium carbonate, nearly half have more than 1 per cent., one-fifth have more than 2 per cent., a considerable number over 4 per cent., and a few isolated cases carry over 10 per cent. of calcium carbonate in the raw coal. Since decomposition of $CaCO_3$ is rapid at 900° C. and evident at 600° it is apparent that in coals of this type care must be taken to determine the actual amount of $CaCO_3$ present. Parr has also shown that sulphate in the form of ferrous or ferric sulphate is present in fresh coal in amounts varying from a few tenths up to 1 per cent. and that this amount increases rapidly in the finely ground portions of the laboratory sample. With coals high in lime this sulphate on ignition for ash probably becomes calcium sulphate, as does also the sulphur of pyrites.

The 1913 report of the Committee on Coal Analysis recommends the following method for the determination of ash.

[1] *Jour. Ind. and Eng. Chem.*, 5, 523 (1913). Ill. State Geological Survey, *Bul.* 16, p. 242.

"Unless the coal is of a type known to be free from carbonate the amount of carbon dioxide must be determined. A 5-grm. sample, recently boiled distilled water and dilute hydrochloric acid are employed, making use of any convenient apparatus for collecting, absorbing and measuring accurately the carbon dioxide discharged from the coal. It is most convenient to obtain the factor as in the form of carbon.

"One gram of coal, either freshly weighed or that which has been used for the moisture determination, is ignited in a shallow capsule or porcelain crucible by placing directly in a muffle maintained at a dull or cherry-red temperature between 700 and 750° C. and retained at this temperature for 20 or 30 minutes or until all of the carbon is burned out. The capsule is cooled in a desiccator and weighed. In the absence of a muffle the desired temperature may be obtained by placing the capsule at first just above the tip of a Bunsen flame turned down to about 2 or 3 in. in height. After the larger part of the carbon is burned off in this manner the flame is increased so that the tip comes well into contact with the bottom of the capsule.

"For coals having carbon dioxide present in an amount to exceed 0.2 per cent., the ash after cooling is moistened with a few drops of sulphuric acid (diluted 1 : 1) and again carefully brought up to 750° C. and retained at that temperature for three to five minutes. The capsule is cooled in a desicator and weighed. Three times the equivalent of carbon present as carbon dioxide is subtracted from the ash as weighed in order to restore the weight of the calcium sulphate formed to the equivalent of calcium carbonate."

The appearance of the ash gives some indication of its fusing point and hence its tendency to form clinkers. The largest constituents in ash are silica and alumina, all of whose compounds have relatively high melting-point and are white in color. Iron oxide colors ash red and reduces the melting-point of the alumina silica series markedly. Therefore a red ash indicates low melting-point and trouble with clinker while a white ash indicates high melting-point. This rule fails with coals such as those from Illinois which carry material amounts of lime, for the lime reduces the melting-point without giving a color. However, the Illinois coals usually carry enough iron to give a red color as well.

9. Fixed Carbon.—Fixed carbon is obtained by adding together the weights of moisture, volatile matter and ash and subtracting this sum from the weight of the initial sample. Since the amount

of fixed carbon is obtained by difference, proximate analyses of coal always add up to an even 100 per cent. The percentage of fixed carbon plus ash gives a fair indication of the amount of coke which would be obtained from a coal. An indication of the quality of the coke may be obtained from an examination of the residue remaining after the determination of volatile matter. Good coking coals give a button of hard dense coke. Feebly coking coals give a cracked and weak button while non-coking anthracites and lignites give a powdery or granular residue.

10. Sulphur.—The estimation of sulphur is usually considered as part of a proximate analysis although it is estimated separately and its percentage is not included in the 100 per cent. formed by the sum of the moisture, volatile matter, fixed carbon and ash. Sulphur usually exists in coal as pyrites FeS_2, but part of it may exist in combination with carbon compounds, part even as free sulphur and especially in weathered coals as calcium sulphate or sulphate of iron. No attempt is ordinarily made to distinguish between these various forms of sulphur. The coal is treated with an agent which finally brings all forms of sulphur into a soluble sulphate form. This is then precipitated as barium sulphate and calculated back to sulphur. The method recommended in 1899 by the American Chemical Society was a modification of that proposed by Eschka in 1874.

The committee on Coal Analysis in its 1913 recommendations adopts the report presented by Barker[1] permitting the use of three alternative methods which have shown themselves to be accurate. The methods are:

(*a*) the Eschka method.
(*b*) the Atkinson method of fusion with sodium carbonate.
(*c*) the method of fusion with sodium peroxide.

The Eschka method is recommended in substantially the same form as in the standard method of 1899. The substitution of copper oxide for magnesium oxide in the method gives more rapid combustion but it has been objected to on the ground that the black specks of copper oxide look so much like free carbon that it is difficulty to tell when the coal is completely burned. The following details of the Eschka method are from the Committee's report.

[1] *Jour. Ind. and Eng. Chem.*, 5, 524 (1913).

"*The Eschka Method.*—The essentials of this method as described by G. L. Heath[1] have been modified as given in the former report of the Committee of the American Chemical Society on Coal Analysis.[2] Additional directions for application when city gas is used are also included in the method herein recommended.

"Thoroughly mix on glazed paper 1.3737 grm. of coal and 6 grm. of Eschka mixture. This mixture is prepared by thoroughly incoporating two parts magnesium oxide with one part of sodium carbonate by passing through a 40-mesh screen. By this method of preparation the mixture attains a uniformity comparable with that of the laboratory sample of coal and thorough incorporation is, therefore, more easily effected. Transfer to a No. 1 Royal Berlin porcelain crucible and cover with about two grams of the Eschka mixture. On account of the amount of sulphur contained in artificial gas, it is preferable to heat the crucible over an alcohol, gasoline or natural gas flame or in an electrically heated muffle. Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of sulphur. Heat the crucible slowly for about 30 minutes, gradually increasing the temperature and occasionally stirring until all black particles disappear, which is an indication of the completeness of the procedure.

"The use of artificial gas for heating the coal and Eschka mixture is permissible, provided the crucibles are heated in a muffle and a blank determination of the amount of sulphur absorbed from the gas is made. Place a crucible in a cold gas muffle and gradually raise the temperature to about 870° or 925° C. (cherry-red heat) in about one hour. Maintain this maximum temperature for about one and a half hours and then allow the crucible to cool in the muffle. Remove and empty the contents into a 300 c.c. beaker and digest with 200 c.c. of hot water for one-half to three-quarters of an hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate amounting to about 250 c.c. with 10 to 20 c.c. of saturated bromine water and make slightly acid with concentrated hydrochloric acid. Transfer the beakers to the hot plate and, upon boiling, precipitate the soluble sulphates by adding slowly from a pipet with constant stirring 10 c.c. of a hot 10 per cent. solution of barium chloride. Continue boiling for fifteen minutes and allow to stand for at least two hours

[1] *J. Am. Chem. Soc.*, 20, 630.
[2] *Ibid.*, 21, 1127.

at a temperature just below boiling. Filter through an ashless filter paper and wash first with hot water containing 1 c.c. of hydrochloric acid per liter and then with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulphate in a weighed platinum or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. The paper should be smoked off gradually at first. After the paper is practically consumed raise the temperature to approximately 925° C. and heat to constant weight. In case artificial gas is used as a heating agent, a blank to correct for contamination due to sulphur in the gas is carried through the process in the manner described above, using the same amounts of Eschka mixture, wash water, bromine water, hydrochloric acid and barium chloride solution as employed in the regular determination. A large number of tests using a mixed coal and carburetted water gas containing not more than 25 grains of sulphur per 100 cu. ft. show blanks averaging 0.003 grm. of barium sulphate. These blanks include the impurities in the form of sulphur compounds in the reagents, which amount to nearly one-half of the total weights. The percentage of sulphur is obtained by deducting the blank, provided artificial gas is used, and multiplying the resulting figures by 10."

The Peroxide Fusion Method.—The decomposition of coal by fusion with sodium peroxide was first proposed by Parr[1] for calorimetric purposes. The reaction was adapted to the estimation of sulphur by Sundstrom[2] and later modified by Pennock and Morton[3], and Parr[4]. The method is entirely reliable and is much more rapid than the Eschka method.

When a mixture of a dry combustible substance and sodium peroxide in proper proportions is ignited by a hot iron wire, the mass fuses with very little spattering and the sulphur, no matter what its initial form of combination, is converted to a soluble sodium sulphate. If the coal is damp or the proportions are not correct there may be violent spattering so the reaction should be carried out in a closed vessel. The residue from the determination of heating value in the Parr calorimeter is of course available at once for the estimation of sulphur. Where a separate

[1] *J. Am. Chem. Soc.*, 22, 646 (1900).
[2] *J. Am. Chem. Soc.*, 25, 184 (1903).
[3] *J. Am. Chem. Soc.* 25, 1265 (1903).
[4] *J. Am. Chem. Soc.*, 30, 767 (1908).

combustion for sulphur is to be made a simple crucible of steel or brass provided with a perforated cover which may be clamped in place is used, as shown in Fig. 42. For a charge of 0.7 grm. bituminous coal about 16 grm. of sodium peroxide are required while for the same weight of coke or anthracite about 12 grm. of peroxide are best. The charge is mixed, the cover clamped on and the crucible placed on a support in a pan of water, so that its lower half is immersed and yet there is free circulation of water around the bottom. The charge is fired by a stiff iron wire which is heated to redness and thrust through the hole in the cover. If the reaction proceeds properly almost no flame will issue from the hole. If the proportions are not correct there may be considerable spattering so that the operator should stand at arms length from the crucible when inserting the wire. If the first explosion is too violent, add more sodium peroxide which acts as a diluent. If, on the other hand, combustion has been incomplete as shown by soot on the inside of the lid of the crucible, decrease the amount of sodium peroxide on the next attempt. If there is difficulty in obtaining ignition as is sometimes the case with coke and especially with ashes, add an accelerator. Parr recommends the following fusion mixture: 10 grm. sodium peroxide, 0.5 grm. potassium chlorate, 0.5 grm. benzoic acid.

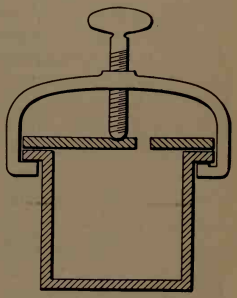

FIG. 42.—Crucible for peroxide fusion.

To dissolve the fused mass, place the crucible and cover in about 200 c.c. of distilled water. Rinse off the crucible, acidify slightly with HCl, filter out any insoluble matter and proceed with precipitation of $BaSO_4$ as in the Eschka method.

The details of the Atkinson method as recommended by the Committee on Coal Analysis are as follows:

The Atkinson Method.[1]—"Thoroughly mix on glazed paper 1 grm. of the laboratory sample of coal with 7 grm. of dry sodium carbonate and spread evenly over the bottom of a shallow platinum or porcelain

[1] *J. Am. Chem. Soc.*, 21, 1128 (1899).

dish. Place on a triangle slightly elevated above the bottom of a cold muffle. Raise the temperature of the muffle gradually until a temperature of 650° to 700° C. (dull red heat) has been obtained in half an hour and maintain this temperature for ten or fifteen minutes. The sodium carbonate should not sinter or fuse. The mixture should not be stirred during the heating process. When the dish has cooled sufficiently to handle, the matter should be examined for black particles of unburned carbon and in case such indications of incompleteness of the process appear, the dish should be replaced and heated for a short time. When all carbon is burned, remove the dish and digest the contents with 100 to 125 c.c. of warm water. Allow the insoluble matter to settle, decant through a filter and wash several times by decantation. Transfer to the filter, adding a few drops of a solution of pure sodium chloride, if the insoluble matter tends to pass through the filter. The washing should be continued until the filtrate shows no alkaline reaction. Make the filtrate slightly acid with sufficient concentrated hydrochloric acid and precipitate the sulphates with barium chloride as described under the Eschka method. No oxidizing agent is required."

Sulphur may also be determined in the water rinsed from the bomb calorimeter after a calorimetric determination, provided that the calorimeter is provided with a lining which is not attacked by the acid formed. The bomb should be very thoroughly rinsed with hot water, the solution filtered and precipitated with $BaCl_2$ as usual. The tendency with this method will be toward low results.

Parr[1] has developed a rapid photometric method for the determination of sulphur in coal. The residue from the fusion with sodium peroxide is dissolved, acidified, diluted, and precipitated cold with a mixture of barium chloride and oxalic acid. The precipitated barium sulphate is in a very finely divided condition so that it does not settle readily. The photometer consists of a graduated tube of special design which rests upon a diaphragm below which is a candle flame. The emulsion of $BaSO_4$ and solution is slowly poured into this photometer until the sharp outline of the flame disappears. The height of solution in the photometer tube gives, by reference to a special table, the per cent. of sulphur in the coal. Results

[1] *Jour. Am. Chem. Soc.*, 26, 1139 (1904); *Jour. Ind. and Eng. Chem.*, 1, 689 (1909).

on 35 coals quoted by Parr show good agreement with gravimetric methods.

11. Ultimate Analysis.—Carbon and Hydrogen.—Carbon and hydrogen in coal and coke are determined as is usual in the ultimate analysis of organic compounds, by combustion in a stream of dry and pure oxygen and absorption of the resulting carbon dioxide and water. The analysis is a difficult one and should not be attempted by one who has not had practice in the general method. If it is necessary for an analyst without training in this particular line to undertake such an analysis he should practice on the ultimate analysis of such pure compounds as sugar and benzoic acid until he has attained proficiency. Detailed directions for these determinations in coal are given in Technical Paper 8 of the Bureau of Mines.

In a determination of the heating value of coal in a bomb calorimeter, there is complete oxidation of the carbon to carbon dioxide and of the hydrogen to water. An absorption train may be connected to the bomb and the gases allowed to bubble slowly through it. After the pressure in the bomb has fallen to that of the atmosphere the bomb may be immersed in a dish of hot water and suction applied to the absorption train. It is in this way possible to estimate the carbon dioxide and water formed in the combustion. Kroeker[1] proposes a bomb which has an inlet and an outlet valve so that dry and pure air may be passed through the bomb after the pressure has been relieved. The method is capable of giving good results in skilled hands. Great care must be taken to keep the packing on the oxygen valves in perfect condition as otherwise part of the products of combustion will escape during the slow process of emptying the bomb. There is also a minor error due to the oxidation of some of the nitrogen to form nitric acid which is reported as carbon dioxide.

Parr[2] has proposed a gas volumetric method of determining carbon from the residue of the peroxide fusion in the Parr calorimeter. The residue consisting largely of Na_2CO_3 and Na_2O_2 is dissolved in water and treated with acid. Carbon dioxide and oxygen are evolved and the carbon dioxide is

[1] *Zeit. d. Vereins f. d. Rübenzuckerindustrie*, 46, 177 (1896).

[2] *University of Illinois Bulletin* Vol. 1, No. 20 (1904).

estimated by absorption. There are a number of minor sources of error which make it difficult to get accurate results by this method. Sodium peroxide both dry and in solution readily absorbs carbon dioxide from the air and care is necessary in order to keep the correction factors constant. Difficulty has also been experienced in completely boiling off the carbon dioxide from the solution.

12. Nitrogen.—The chief value attaching to a knowledge of the per cent. of nitrogen in a coal is the indication which it is believed to give of the amount of ammonia which the coal will yield on destructive distillation. No attempt is usually made to distinguish between the various forms in which nitrogen may exist in coal. The total nitrogen is best determined by the Kjehldahl method or one of its modifications as regularly used in the ultimate analysis of organic compounds. The following details are taken from Techinical Paper 8 of the Bureau of Mines.

"The well-known Kjehldahl method is used in determining nitrogen. One gram of the coal sample is boiled with 30 c.c. of concentrated sulphuric acid (H_2SO_4) and 0.6 grm. of mercury until all particles of coal are oxidized and the solution nearly colorless. The boiling should be continued at least two hours after the solution has reached the straw-colored stage; then crystals of potassium permanganate ($KMnO_4$) are added, a few at a time, until a permanent green color remains. After cooling, the solution is diluted to about 200 c.c. with cold water. Twenty-five cubic centimeters of potassium sulphide (K_2S) solution (40 grm. K_2S per liter) are added to precipitate the mercury; to prevent bumping 1.0 grm. of granular zinc, and, to prevent frothing, a piece of paraffine about the size of a brass 1 grm. weight are also added. Enough saturated sodium hydroxide (NaOH) solution (usually 80 to 100 c.c.) to make the solution distinctly alkaline is next added and the flask is at once connected with the condenser. The ammonia (NH_3) is distilled over into a measured amount of standard sulphuric acid solution, to which has been added sufficient cochineal indicator for titration. The solution is distilled until about 200 c.c. of distillate has passed over, and the distillate is titrated with standard ammonia (NH_4OH) solution (20 c.c. NH_4OH solution = 10 c.c. H_2SO_4 solution = 0.05 grm. nitrogen). The transfer to a distillation flask may be avoided by the use of a 500 c.c. Kjehldahl flask for digestion of the coal, connection being made direct from the Kjeldahl digestion flask to the condensing apparatus."

13. Phosphorus.—Phosphorus is usually determined only in fuels which are to be used for metallurgical processes where the fuel is to come in direct contact with the metal. The following details are those of the Bureau of Mines.

"For the determination of phosphorus in coal or coke, a sample weighing 6.52 grm. is burned to ash in the muffle furnace. The ash is mixed with four to six times its weight of sodium carbonate plus 0.2 grm. of sodium nitrate, and is fused at the highest temperature of the blast lamp. The fused mass is dissolved in water, acidified, and evaporated to dryness. The residue is taken up in hydrochloric acid, and the phosphorus determined in the usual way, either by weighing or by titrating the yellow precipitate with permanganate."

14. Oxygen.—There is no direct method for the estimation of oxygen in coal. In an ultimate analysis the percentages of carbon, hydrogen, nitrogen, sulphur and ash are added and the difference between this sum and 100 per cent. is called oxygen. It is thus apparent that any errors in the estimation of the other constituents are reflected in the figure for oxygen and that therefore this figure is to be regarded as the least significant of the analysis.

15. Methods of Reporting Analyses.—The analysis is usually made on the air-dried sample since the sample in this form is least liable to change. The original figures obtained by the analyst will therefore be for coal in this form. He may now take into account the moisture lost in air-drying and calculate the analysis to a basis of coal "as received," he may mathematically eliminate all the water and report as "Coal free from Moisture," or he may by calculation eliminate both the moisture and ash and report as "Coal free from Moisture and Ash."

Numerous attempts have been made to calculate "true coal" or "coal substance" by elimination, in addition to the moisture and ash, of water of hydration contained in shale, and carbon dioxide contained in carbonates of the ash—both of which are driven off in whole or in part with the volatile matter whereas they really belong to the ash. Such corrections are difficult to apply and are not often made in technical work. If any event the data reported should be sufficient to allow a recalculation of the results to any other basis. Ordinarily the air-drying loss and analysis of air-dried coal are reported since they are the figures

actually obtained by the analyst and in addition whatever other forms of report may be called for. The following analysis of a Pittsburg coal shows the form of report.

PERCENTAGE COMPOSITION OF COAL

Proximate analysis	Air-dried	As received	Calculated moisture-free	Calculated moisture and ash-free
Moisture	1.07	3.94		
Volatile matter	34.55	33.55	34.93	37.13
Fixed carbon	58.51	56.81	59.14	62.87
Ash	5.87	5.70	5.93	
	100.00	100.00	100.00	100.00
Ultimate analysis				
Hydrogen	5.16	5.33	5.09	5.41
Carbon	79.52	77.21	80.38	85.44
Nitrogen	1.41	1.37	1.43	1.52
Oxygen	6.97	9.35	6.09	6.48
Sulphur	1.07	1.07	1.08	1.15
Ash	5.87	5.70	5.93	
	100.00	100.00	100.00	100.00
Air-drying loss	2.90			

16. Accuracy of Results.—It will be evident from a consideration of this chapter and the preceding one on sampling that the error in sampling is liable to be larger than the error of analysis. The Joint Committee on Coal Analysis in its 1913 report estimates the allowable variations under its new methods of analysis as follows:

	Same analyst, per cent.	Different analysts, per cent.
Moisture, under 5 per cent	0.2	0.3
Moisture, over 5 per cent	0.3	0.5
Volatile matter, bituminous coals	0.5	1.0
Volatile matter, lignites	1.0	2.0
Ash, no carbonates present	0.2	0.3
Ash, carbonates present	0.3	0.5
Ash, more than 12 per cent	0.5	1.0
Sulphur, in coal	0.05	0.1
Sulphur, in coke	0.03	0.05

The greatest variation is in the volatile matter and when a contract is to be awarded in which an accurate determination of volatile matter is demanded, it is advisable for the purchaser and the bidder to jointly analyze a single sample of coal and harmonize their differences in analytical procedure before the contract is awarded. Lord,[1] from his wide experience, states that in ultimate analysis the accuracy can be safely stated as within 0.05 per cent. in the case of hydrogen, perhaps 0.3 per cent. on carbon, 0.03 per cent. on nitrogen and 0.05 per cent. on sulphur.

17. Slate and Pyrites.—It is frequently desirable to determine how much of the pyrites and slate is in a form which will permit mechanical separation by coal-washing or otherwise. Lord[2] recommends the use of calcium chloride solutions with which a specific gravity as high as 1.35 may be obtained or zinc chloride solutions with which a specific gravity of 2.0 may be reached. The coal is tested by crushing to various degrees of fineness and determining the differences in composition of the portion which floats and that which sinks in solutions of varying specific gravities.

[1] *Jour. Ind. and Eng. Chem.*, 1, 307 (1909).
[2] *Jour. Ind. and Eng. Chem.*, 1, 308 (1909).

CHAPTER XVI

HEATING VALUE OF COAL BY THE BOMB CALORIMETER

1. General Methods of Determining Heating Value.—The heating value of a fuel is determined either directly in a calorimeter or indirectly by calculation from its chemical composition. The direct calorimetric method involves the combustion of the fuel by oxygen supplied either as free oxygen gas or as combined oxygen of some chemical compound, the operation being carried out in a closed vessel immersed in a known mass of water under conditions which ensure that the heat evolved in the oxidation shall be with as little loss as possible transferred to and retained by the calorimetric vessel and the water. The heat evolved is calculated from the rise in temperature of the system.

Modern methods of calorimetry really commenced with the invention by Berthelot of his bomb calorimeter described in 1881.[1] This has become the standard method for the determination of heating values and therefore the whole of this chapter is devoted to it. Other methods, especially that of Parr, are described in the following chapter.

2. The Bomb Calorimeter.—Berthelot showed that if combustion of carbon compounds took place in a closed vessel in an atmosphere of oxygen compressed to at leat seven atmospheres and with a weight of combustible such that only 30 to 40 per cent. of the oxygen initially present was consumed, combustion was rapid and complete. His bomb was lined with heavy platinum and was very expensive. Hempel in the second edition of his gas analysis published in 1889 described a much cheaper bomb which had no lining at all. His modification has been found by the author to be mechanically unsatisfactory. The neck of the bomb is constricted so that it is difficult to dry the interior, and the headpiece is threaded and screws *into* the neck roughening the lead

[1] *Annales de Chimie*, 5 Serie, 23, 160 (1881). *Annales de Chimie*, 6 Serie, 6, 546 (1885).

gasket as it turns upon it. The method of making connection to the oxygen tank is also unsatisfactory.

Mahler[1] in 1892 reported a careful study of Berthelot's method as applied to coals, and described a bomb of improved construction with an enamel instead of a platinum lining. This bomb is mechanically better than Hempel's, but there is still the objection that the top as it screws down, roughens the gasket.

Atwater[2] in 1894 described a modification of the bomb calorimeter distinctly superior mechanically to the preceding forms. It resembled more closely the Berthelot bomb than either of the others but, whereas the Berthelot bomb was closed by a tapered plug held in place by a screwed cap, Atwater's was closed by a flat cap held in place by a collar slipped over it and screwed over threads on the outside of the bomb after the manner of a union pipe-fitting. In this way all tearing of the gasket was avoided. The Atwater bomb may be provided with a gold or platinum lining and is to be regarded as the highest type of instrument for research work.

Many modifications of the bomb calorimeter have been made by other workers, but the principle has not been changed. Anyone familiar with one instrument can readily learn to use any other.

3. Details of the Bomb Calorimeter.—The bomb calorimeter which has been in use in the calorimeter laboratory of the University of Michigan since 1908 is shown in Figs. 43 and 44. It is in general patterned after the Atwater bomb, but possesses several improvements. One of these, due to Mr. Edwin H. Cheney, is the octagonal belt on the body of the bomb which fits into a recessed plate and holds the bomb rigidly while the cover is being screwed on. Another, due to Professor S. W. Parr, is the deeply recessed groove for the gasket in the cover of the bomb into which the straight lip of the bomb fits closely so that a rubber gasket may safely be used. Improvements in various details are due to Mr. J. H. Stevenson, instrument maker of the University of Michigan. Details of the bomb are shown in Fig. 43. It consists of a cylinder of about 300 c.c. capacity

[1] *Bul. de la Societe d. Encouragement*, 1892, 319.

[2] *Starrs Conn. Experiment Station Report*, 1894, 135; also *J. Am. Chem. Soc.*, 25, 659 (1903).

machined from a solid block of steel. On this sits a cover carrying the oxygen inlet and needle valve, also machined from a solid piece of steel. The cover is pressed tightly into place on the bomb by a heavy ring cap screwing over it and drawn up tightly by a spanner. Compressed oxygen is admitted through a flexible metal tube soldered at A to the steel tube with the coned head B. This tube AB slides freely in the threaded sleeve C. Its coned head makes a gas tight joint with the bomb when C

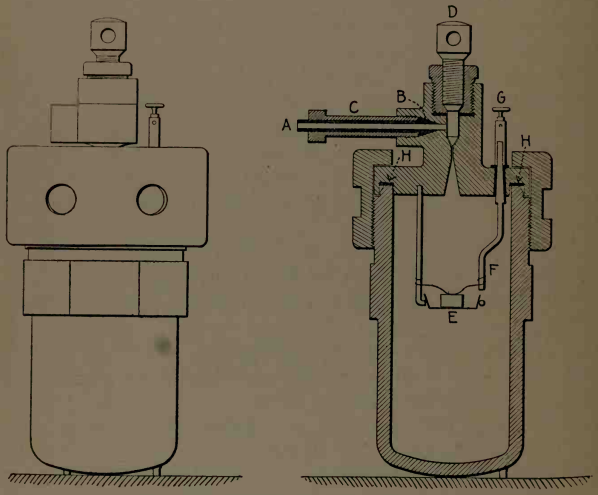

FIG. 43.—Details of calorimetric bomb.

is screwed up. The needle valve D closes the bomb when it is screwed down. The coal sits in a flat nickel capsule E supported on a brass ring which screws into the head piece. The insulated electrical connection FG is a brass rod coned where it passes through the head piece from which it is insulated by a bit of thin rubber tubing. The binding post G screwing down on the threaded end of F which projects through the cover pulls the cone tightly into its seat and makes a gas tight joint. A mica disc placed between the binding post and the bomb completes

the electrical insulation of the electrode from the bomb. The gasket which fits into the groove H may be of lead, hard fiber or rubber. Rubber gives a tight joint with the least pressure of the spanner and is therefore to be preferred. If it is cut to fit the groove accurately the inner lip of the bomb projecting into the recessed head will effectually protect it from the hot gases evolved in the bomb during combustion.

Fig. 44 shows the various parts of the calorimeter. Two bombs are shown, one assembled and one taken apart and with the head sitting on a stand in position for adjustment of the fine iron

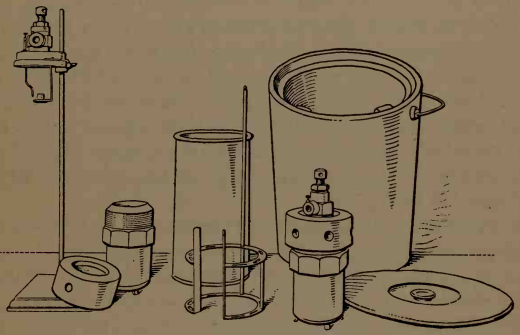

FIG. 44.—Bomb calorimeter.

firing wires. The nickel-plated copper can, the stirrer and the insulating buckets are also shown.

The insulating buckets as shown in Fig. 44 consist of two concentric fiber pails with air in the space between them. It is in many ways preferable to have this space filled with water, whose temperature may be set at any desired point. This minimizes the effect of draughts in the room and enables the operator to use a Beckman thermometer without having to shift its zero when the room temperature fluctuates. The temperature of the water must not, however, be so far below room temperature that dew will deposit on the walls of the calorimeter vessel. When a water jacket is thus used in the calorimeter, it should be provided with a stirrer and its temperature should be recorded.

4. Thermometers.—Thermometers for the calorimeters should be made especially for the purpose with a stem below the graduations long enough to allow the bulb of the thermometer to be opposite the center of the bomb. The entire length of the graduated portion of the thermometer should be visible above the calorimeter lid. It is necessary that it be possible to read the rise in temperature to at least 0.01° C. The best thermometers are those of the Beckman type with a scale length of 6° and a zero point adjustable between 12° and 25°. This type of thermometer is always to be recommended where the calorimeter room is of relatively constant temperature so that it is not necessary to change the zero point often. Where this desirable condition is not fulfilled calorimetric thermometers with a fixed scale running from 15° to 30° C. must be used. These are usually divided only into 0.02° to avoid the excessive length of stem which would otherwise result. The thermometer should in any case have been carefully calibrated since an error of 0.01° on the average rise of 3° means 0.3 per cent. or approximately 40 B.t.u. per pound of coal.

5. Preparation of Sample.—The methods to be followed in obtaining a representative sample from a large quantity of coal and the precautions necessary in grinding, sampling and drying this large sample have been given in Chapters XIV and XV. It is assumed here that the sample is already ground to a fineness of at least 60-mesh and has been air-dried. The amount of moisture is immaterial so far as the operation of the bomb calorimeter is concerned, but an air-dried sample is less likely to change during the operation of weighing.

When powdered bituminous coal is burned in compressed oxygen, combustion is so violent that there is danger that gas and even solid particles will be projected unburned through the flame zone. The rate of combustion may be materially lessened by reducing the surface of coal exposed to the oxygen. This is best accomplished by briquetting the coal. Most bituminous coals may be readily compressed into pellets in a screw press. The pressure should be slowly applied and allowed to remain for a few minutes. The resulting pellet may be trimmed to approximate weight with a penknife. It is advantageous to break it into two or more pieces and discard the dust before weighing. The

advantage of cutting the pellet lies in the readier ignition, for pellets which have been pressed very hard are sometimes so dense on the surface that they fail to ignite. It is possible to compress some bituminous coals so firmly on the surface that the gas evolved in the interior of the briquette by destructive distillation explodes the briquette and blows a cap of coke out of the crucible. If these dense briquettes are cut into several pieces, as directed above, the trouble will be obviated. It is not necessary to briquet anthracite coals or coke. Indeed, it is not possible to do so without the addition of a binder such as sugar or bituminous coal.

6. Manipulation of Bomb Calorimeter.—The bomb is taken apart and examined to see that it is in good condition and that the gasket is not cut. A few drops of water are placed in the bottom part of the bomb which is set in its receptacle in the table-top. The top part of the bomb is placed on a ring of an ordinary ring stand as shown in Fig. 44 which allows the heavy terminals to drop through in a convenient position for adjustment of the fuse wire and sample. The weighed sample of coal is placed on a shallow thin nickel or platinum capsule resting on the supporting ring suspended from the head of the bomb. The capsule must be almost flat to allow free access of oxygen from the edges as the flame flares up. Otherwise combustion may be incomplete. It must be thin or it will chill the flame and prevent complete combustion. It is advisable with anthracite and coke to place a thin pad of ignited asbestos on the capsule in order to decrease still further the cooling effect of the metal.

A measured length, preferably not more than two inches, of the fine iron ignition wire 34 B. & S. gage is attached to the heavy wire terminals by winding the ends of the fine wire several times around the heavy ones, leaving the fine wire in the form of a loop between the terminals. After making connections the loop is pushed down until it rests on the fragments of coal. Care is to be taken that the wire does not touch the metal capsule and form a short circuit.

The cover with the sample in position is placed carefully on the bomb and the threaded collar slipped over it and screwed down, pressure finally being applied with the spanner. A novice will nearly always screw the cover down harder than

necessary, thus shortening the life of the gasket. A moderate pressure will suffice if the gasket is a good one. Gaskets cut from ordinary red fiber packing are too porous to be tight unless screwed down with great pressure. They may be much improved by vacuum impregnation with a solution of 5 grm. of glue in 5 c.c. of glycerine and 100 c.c. of water. After impregnation the gaskets are to be dried in air and rubbed with a piece of paraffine to keep them from sticking to the metal.

The loose joint on the end of the flexible metal tube from the oxygen tank is screwed into the head of the bomb, the needle valve of the bomb opened at least a full turn, and then the valve on the oxygen tank is opened slightly, the gas entering in a slow stream from the tank until the gage shows 20 atmospheres pressure. If the valve on the tank is opened relatively more than the one on the bomb the gage between the two may show 20 atmospheres before there is that much pressure in the bomb. The oxygen valve on the tank is to be closed first and after that the valve on the bomb. If the valve on the bomb is closed before that on the tank, the pressure on the gage will rise very quickly to the full pressure of the oxygen tank which may be 2000 lb. and the gage may be blown up.

The bomb is disconnected and placed in the water of the calorimeter or in a separate vessel of water to test for leaks. If bubbles of gas appear around the threaded ring the cover must be screwed down more tightly, and possibly the gasket may have to be replaced. If bubbles of air come from the head it is evident that the needle valve is leaking. It is worse than useless to try and force it to become tight by screwing down the needle with great pressure. A needle valve truly ground into its seat is tight with slight pressure. If a particle of grit comes between the metal surfaces the application of pressure causes it to scour the polished surface and the valve will leak until it has been again ground to a true surface. In case of a leaking needle valve the pressure must be relieved, the bomb opened and the needle valve unscrewed entirely out of the head. The lock nut into which it was threaded is also to be removed. The coned seat into which the needle valve is ground may now be seen in a strong light. The best policy is to grind the needle valve into its seat, an operation requiring not more

than ten minutes if the valve has not been abused. The needle valve is dipped into a paste of fine emery or carborundum in water and ground into its seat by rotating it back and forth with the fingers. A polished ring will soon be visible on the cone point and a corresponding ring in the seat. When this appears, unless the metal has been badly scratched, the process may be considered complete and the grinding interrupted. The valve is to be thoroughly cleaned from grit and dried, when it is ready for use.

The bomb when charged is to be carefully centered in the calorimeter vessel which is in turn centered in the outer vessels. The stirrer and thermometer are placed in position and two liters of water whose temperature is approximately 3° below room temperature is added. A glass flask which holds 1000 c.c. of water, contains the following weights of water, when balanced against brass weights in air.[1]

15° C.	998.05 grm.
20° C.	997.18 grm.
25° C.	996.04 grm.
30° C.	994.66 grm.

The liter flasks of various makers differ in the amount of water which they discharge and the flask should be calibrated by direct weight for some one temperature. It is more convenient for calculation purposes to calibrate the flask to deliver 2000 grm. of water at the temperature most frequently used, or sometimes to deliver such an amount of water that the sum of the water added and the water value of the calorimeter shall be 2500 grm. It is in many ways better to weigh the water directly into the counterpoised calorimeter vessel as it sits on the balance.

Especial care is to be taken to see that the thermometer is centered in the space between the bomb and the edge of the vessel. If it touches either, or even if it is a little off center the rise of the thermometer will not be even and the result may be in error.

After the adjustments are complete the stirrer is operated for at least two minutes before the first temperature reading

[1] *Bureau of Standards Bull.* 4, 600 (1907–08).

is made on an even minute. Readings are to be made each minute thereafter for at least five minutes, the stirrer being kept going steadily at 30–40 strokes per minute and the temperature slowly and steadily rising with each reading as heat is absorbed from the air of the room, or dropping if the calorimeter is above room temperature. This ends the preliminary period, which must show at least five readings changing by regular increments due solely to heat transfer to or from the outside air.

The firing circuit is closed simultaneously with the last reading of the preliminary period. The iron wire becomes heated to redness, the coal ignites and the iron wire fuses almost instantly. It is well to have an electric lamp in the firing circuit which lights when the current is turned on and is extinguished when the wire fuses. An ammeter in the circuit answers the same purpose showing that the ignition is prompt and that an undue amount of heat is not imparted to the calorimeter by the electric current. Current for ignition may best come from a storage battery or group of dry cells giving about 12 volts. Higher voltages are apt to cause insulation troubles.

Within a half minute after ignition the thermometer begins to rise so rapidly that it is not possible to make the thermometer readings accurately. They should be taken as accurately as possible, and regularly on each minute. After about three minutes the thermometer reaches its maximum, but the stirring and temperature readings must be kept up without intermission for a total of ten minutes after ignition to obtain data for the radiation corrections.

After the termination of the thermometer readings the bomb is removed from the calorimeter, wiped dry, and placed in its receptacle on the table. The needle valve is opened and after the pressure is relieved the top is removed. The coal should be perfectly burned and the ash should appear as fused beads. The iron wire has burned as far as the heavy conductors and in accurate work the length of the wire unburned should be determined to enable the proper correction to be made for the weight of wire burned. The weight of wire burned comes to be almost a constant for each operator and may be taken as such in ordinary work. If soot appears in the bomb or on the capsule, the determination should at once be rejected. With inexperienced ope-

rators this trouble is frequently caused by opening the valve on the oxygen tank too fast when filling the bomb, with the result that the gage on the connecting tube jumps to the proper reading before the indicated pressure is reached in the bomb. If trouble persists it may be necessary to increase the oxygen pressure to 25 atmospheres. The bomb is to be rinsed out carefully and unless it is to be used again at once, is to be dried best in an oven at a temperature of about 35–40° C. If the bomb is not dried in this way rust is almost certain to form in the needle valve and prevent it from closing tightly.

7. Thermometer Corrections.—The calorimetric thermometer should have the certificate of the Bureau of Standards. In addition to the corrections indicated on the certificate as inherent in the thermometer on account of variation in the diameter of the capillary tube, etc., minor corrections must be made in accurate work for variations due to the conditions under which the thermometer is used. The Bureau of Standards calibrates thermometers when totally immersed in a bath of the temperature indicated. In calorimetric work the bulb and part of the stem is within the calorimeter, while part of the stem projects through the cover of the calorimeter into the air of the room. A small correction must be made for this emergent stem. In the case of Beckmann thermometers an additional "setting factor correction" must be used in case the thermometer is set for a different zero from that used in the calibration. The formulæ for these corrections vary with different sorts of glass and are given in full in the certificate of calibration accompanying each thermometer. The corrections rarely amount to more than a few thousandths of a degree.

8. Radiation Corrections.—The combustion of the coal in a bomb calorimeter is probably a matter of only a few seconds, but it requires several minutes for the heat to be transmitted to the water and for the thermometer to register the rise in temperature. Adiabatic calorimeters have been constructed,[1] but they are not technical instruments. With the usual type of instrument radiation corrections must be made in spite of careful jacketing of the calorimeter. Their magnitude is lessened by adjusting the temperature of the water placed in the calorimeter with reference to

[1] Richards and Jesse, *J. Am. Chem. Soc.*, 32, 268 (1910).

room temperature and to the rise in temperature expected. If the rise in temperature is to be 3°, the water poured into the calorimeter should be about 3° below room temperature. When equilibrium is reached at the time of ignition the temperature will be about 2.5° below that of the room and after combustion it will be about 0.5° above room temperature. This arrangement minimizes the errors. The temperature rises very rapidly after ignition to one so nearly that of the room that changes due to radiation are slight and repeated readings may be made to obtain the final temperature. If the final temperature of the calorimeter is slightly above that of the room there should be a maximum point in the thermometer readings with a slow decrease thereafter.

It is common practice to consider that the maximum thermometer readings represent the actual maximum temperature of the calorimeter, but it is not a safe assumption, for if the thermometer bulb is unduly close to the bomb or if the stirring is inefficient the thermometer may rise too high and fall rapidly again to the temperature representing the true average value of the system, after which it will change slowly and regularly through radiation. It is, therefore, unsafe to use the maximum temperature in calculations. The final temperature of the combustion period should be taken only after sufficient time has elapsed so that it is certain that the system has come to equilibrium. Five minutes is usually sufficient.

Radiation corrections are based on the principle that the interchange of heat between the room and the calorimeter is proportional to the difference in the temperature between them. The temperature of the room is assumed to be a constant during any one operation and need not even be known. The formula for the correction as used by Regnault and developed by Pfaundler[1] is somewhat complicated in appearance, but is simple in use.

Regnault-Pfaundler Formula.—Three sets of temperature readings are to be made. The initial set must not start until after the temperature of the calorimeter has commenced to change regularly due to radiation. It consists of at least five readings made one minute apart. Only the first and last readings and the time interval enter into the calculation, but it is advisable to

[1] *Poggendorf's Annalen*, 129, 115 (1866).

record the intermediate readings as a check on the accuracy of the two important ones and to make sure that the change of temperature is uniform as it should be. At the moment of taking the final reading of the initial period the firing key is pressed and the reading just taken is recorded, both as the final reading of the initial period and the first reading to the combustion period. It is to be marked T_0.

During the combustion period readings are to be made and recorded regularly not only till the thermometer reaches its maximum, but also till it is certain that the changes in temperature are again due solely to radiation. This period may be five

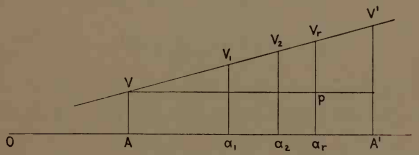

FIG. 45.—Diagram showing derivation of Regnault-Pfaundler formula.

to ten minutes. There follows a final period of five minutes to fix the radiation losses for the latter portion of the test.

The derivation of the Regnault-Pfaundler formula is as follows:

Let t = mean temp. of initial period.
t' = mean temp. of final period.
v = loss per time interval in initial period.
v' = loss per time interval in final period.
T_0, T_1, T_2, T_n = temperature readings in combustion period.
t_1, t_2, ... t_n = average temp. of each interval during combustion period; *i.e.*, $t_1 = \frac{T_0+T_1}{2}$, etc.

The special case assumed by Pfaundler is one where the initial temperature is only slightly different from room temperature, giving a small value for v. The final temperature is considerably above room temperature and the value of v' is larger than v. The geometrical construction for the Regnault-Pfaundler formula is shown in Fig. 45. The demonstration is as follows:

Lay off $OA = t$.

Lay off $OA' = t'$.

Lay off $Oa_1 = t_1$. $Oa_2 = t_2$ . . . . $Oa_n = t_n$

At A erect perpendicular $AV = v$.

At A′ erect perpendicular $A'V' = v'$.

Join V and V′ by a straight line and at a_1 a_2 . . . . a_n erect perpendicular intersecting VV′.

Any ordinate $a_r V_r = AV + {}_pV_r$.

On account of similar triangles $pV_r = \frac{A'V' - AV}{AA'} pV$.

$$a_r V_r = AV + \frac{A'V' - AV}{AA'} pV.$$

$$= v + \frac{v' - v}{t' - t}(t_r - t).$$

C = the algebraic sum of all the ordinates = correction sought.

n = the number of observations in the combustion period proper.

$$C = nv + \frac{v' - v}{t' - t}(t_1 + t_2 \ldots . \ t_n - nt).$$

$$= nv + \frac{v' - v}{t' - t}(T_1 + T_2 + T_3 \ldots . \ T_{n-1} + \frac{T_0 + T_n}{2} - nt).$$

Heat received by the calorimeter from the outside air is considered as negative and therefore in the especial case assumed by Pfaundler where the initial temperature was slightly under room temperature v was negative.

The correctness of the formula is independent of the relative values and signs of v and v′.

The corrected rise in temperature of the calorimeter

$$R = T_n - T_0 + C$$

The need of an elaborate correction for radiation is naturally less when the calorimeter is provided with an adequate stirrer so that the heat interchange between the bomb and the water is quickly effected, and also less when the insulating jacket is good than when it is poor. With a well designed calorimeter the largest part of the rise in temperature occurs in the first minute and if the final temperature is only slightly above room temperature radiation in succeeding minutes is almost negligible.

SAMPLE OF RECORD

Determination of Heating Value of Coal in Bomb Calorimeter.

Sample No. U. 38 Date Nov. 10,
Calorimeter No. 2 Thermometer No. 4
Water Value of Calorimeter 475 grm.
Water Used 2000 c.c. = 1995 grm.
Total water equivalent 2470 grm.

Sample of coal (air-dried) 0.9922 grm.
Thermometer readings

by minutes		Factors
19.68		v = −0.0025
19.68		v′ = +0.0025
19.69		t = 19.69
19.69		t′ = 23.11
19.69	T_0	
21.4	T_1	$T_1+T_2+T_3+T_4=90.0$
22.58	T_2	
22.95	T_3	$\frac{T_0+T_5}{2}=21.4$
23.09	T_4	
23.11	T_5	
		n = 5
23.11		
23.11		Thermometer corrections
23.10		T_n = 23.11 − 0.045 = 23.065
23.10		T_0 = 19.69 − 0.040 = 19.65

$$C=5\times-0.0025+\frac{0.0025+.0025}{23.11-19.69}(90.0+21.4-5\times19.7)=+0.006^\circ\text{ C.}$$

R = 23.065 − 19.65 + 0.006 = 3.421° C.

3.421 × 2470 =		8450 calories
Deduct for 0.025 grm. fuse wire	40	
Deduct for 1.0 per cent. sulphur (20 × .9922) =	20	60
		8390 calories

$\frac{8390}{0.9922}$ = 8455 calories per gram of air-dried coal

8455 × 1.8 = 15,219 B.t.u. per pound of coal.

Proximate Analysis of Coal

Moisture	0.32	per cent.
Volatile Matter	22.87	95.5 per cent.
Fixed Carbon	72.67	95.5 per cent.
Ash	4.14	%
	100.00	

Heat evolved per pound coal dry and free from ash = $\frac{15219}{.955}$ = 15936 B.t.u.

The Dickinson Formula.—H. C. Dickinson of the Bureau of Standards proposes a simpler formula whose derivation has not yet been published. The method of using this formula as published in the preliminary report of the Committee on Coal Analysis is given below.

"Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for four or five minutes before firing, (2) the time (a) at which the last temperature reading is made immediately before firing, (3) the time (b) when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing sixty per cent. of the expected temperature rise, and noting the time when this point is reached), observe (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some five minutes after firing, (5) the final rate of cooling (r_2) in degrees per minute for five minutes.

"The rate r_1 is to be multiplied by the time b − a in minutes and tenths of a minute, and this product added (subtracted if the temperature were *falling* at the time a) to the thermometer reading taken at time a. The rate r_2 is to be multiplied by the time c − b and this product added (subtracted if the temperature were *rising* at the time c and later) to the thermometer readings taken at the time c. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated. This result, corrected for the heats of formation of nitric and sulphuric acids observed and for the heat of combustion of the firing wire when that is included, is to be divided by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the B.t.u. per pound.

Example:

OBSERVATIONS

Water equivalent 2550 grm.
Weight of charge 1.0535
Approximate rise of temp. 3.2°
60 per cent. of approximate rise 1.9°

Time	Temp.	Corrected temp.
10–21	15.244°	(Thermometer corrections from the certificate.)
22	15.250	
23	15.255	
24	15.261	
25	15.266	
(a) 26	15.272	15.276°
	Charge fired	
(b) 27–12	17.2° [1]	
(c) 31	18.500°	18.497°
32	18.498	
33	18.497	
34	18.496	
35	18.494	
36	18.493	

COMPUTATION

$r_1 = 0.028° \div 5 = 0.0056°$ per minute. $b - a = 1.2$ minutes

The corrected initial temperature is $15.276° + 0.0056° \times 1.2 = 15.283°$.

$r_2 = 0.007° \div 5 = 0.0014°$ per minute; $c - b = 3.8$ minutes

The corrected final temperature is $18.497° + 0.0014° \times 3.8 = 18.502°$

Total rise $18.502° - 15.283°$	$= 3.219°$	
Total calories 2550×3.219	$=$	8209
Titration, etc.		− 7
Calories from 1.0535 grm. coal		8202
Calories per gram	7785	
or B.t.u. per lb	14013	

In practice, the time b − a will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

9. Corrections for Oxidation of Nitrogen.—When coal is burned on a grate minute amounts of oxides of nitrogen are formed by the combination of some of the nitrogen of the air and possibly also of the fuel with the oxygen of the air. At the higher temperature of combustion in the compressed oxygen of the calorimeter more oxides of nitrogen are formed and account should

[1] *The initial temperature is* 15.27°; *60 per cent. of the expected rise is* 1.9°. *The reading to observe is then* 17.2°.

be taken of the heat evolved in their formation. The heat of formation of aqeous nitric acid from nitrogen, oxygen, and water is represented, according to Thomsen, by the following equation.

$$2N+5O+H_2O=2HNO_3+29800 \text{ calories.}$$

This corresponds to 1058 calories per gram of nitrogen or 238 calories per gram of HNO_3. The nitric acid formed may be estimated in bombs with platinum or gold linings by rinsing out the bomb and titrating the washings with standard alkali. From this total acidity is deducted the sulphuric acid formed and the balance is considered nitric acid. The amount of nitrogen oxidized is roughly about one per cent. of the total nitrogen present whether introduced as free nitrogen with the oxygen or as combined nitrogen of the coal. The correction is not usually more than 8 calories and may be considered to be offset by the heat absorbed in keeping the gases in the calorimeter at constant volume. (See § 12.)

10. Corrections due to Oxidation of Sulphur.—When sulphur or pyrites burns in the air only about 5 per cent. of the sulphur is oxidized to SO_3, the rest of it remaining as SO_2. When combustion takes place under high oxygen pressure in the bomb calorimeter a much larger percentage burns to SO_3 and correction must be made for it. The equations are:

$$S+2O=SO_2 \text{ gas } +69{,}100 \text{ calories}$$
$$S+3O+H_2O \text{ (excess)} = \text{dilute } H_2SO_4+141{,}100 \text{ calories.}$$

One gram of sulphur burning to SO_2 evolves 2165 calories and to dilute H_2SO_4 evolves 4410 calories. There should therefore be a deduction made of 2245 calories for each gram of sulphur thus oxidized in the bomb. The determination of this oxidized sulphur requires a chemical analysis of the washings from the bomb which adds greatly to the amount of work required. The difficulty is enhanced by the fact that sulphur may be present in coal as free sulphur, as sulphur in organic combination, as pyrites or as calcium sulphate and that the corrections will vary for each of these various forms. For free sulphur burning to H_2SO_4 the correction will be 2245 calories per gram as given above, for sulphur as pyrites 2042[1] calories, while for sulphur as gypsum or sulphate of iron no cor-

[1] Somermeier *J. Am. Chem. Soc.*, 26, 566 (1904).

rection is to be made since it is already in the oxidized form. The situation is further complicated by the fact that free sulphur and sulphur in organic combination do not burn completely to SO_3 in the bomb calorimeter although apparently the sulphur of pyrites does burn completely. It is customary to assume that all of the sulphur in coal exists in the form of pyrites and to deduct two calories for each milligram of sulphur in the sample of coal. This procedure is not above criticism for Parr[1] has shown that the amount of sulphate in fresh coal may be as high as one per cent. and that it doubles after six months storage of the ground sample in the laboratory.

A source of error which should be considered here is that due to the possible action of the dilute sulphuric acid formed upon the inner surface of an unlined bomb. The bomb soon becomes coated with oxide on its inner surface so the action will be between iron oxide and sulphuric acid. According to Thomsen the reaction $Fe_2O_3 \times H_2O + 3H_2SO_4$ (dilute) evolves 33,840 calories. This means 353 calories for each gram of sulphur involved or 3.5 calories as the maximum error involved for 1 grm. sample of a coal containing 1 per cent. of sulphur. The error from this source is totally negligible. An expensive calorimeter lined with gold or platinum is unnecessary except where the greatest refinements of accuracy are sought.

11. Correction Due to Combustion of Iron Wire.—The iron fuse wire which burns to Fe_3O_4 evolves 1600 calories per gram, or 1.6 calories per mg. of iron burned.

12. Reduction to Constant Pressure.—Combustion in the bomb calorimeter takes place at constant volume whereas in ordinary furnace work combustion takes place at constant pressure. Wherever a decrease in volume takes place on combustion as where oxygen unites with hydrogen to form water which condenses, the gases in the calorimeter which should normally have contracted after combustion have had work done upon them to keep them at constant volume with the disappearance of an equivalent amount of heat. The correction amounts to 541 calories for each gram molecule of gas which disappears.

When gaseous oxygen combines with carbon to form CO_2 there is no change of volume and hence no correction. The oxygen in

[1] Jour. Ind. and Eng. Chem. 5, 523. (1913)

the organic matter of the coal, may for the purposes of this calculation be considered to unite with the hydrogen of the coal to form water. No correction is needed here since both the hydrogen and the oxygen were in the solid state before combustion and the water formed is a liquid.

There is always present in coal an excess of hydrogen over that sufficient to combine with the oxygen and this so-called available hydrogen burns with gaseous oxygen to form water which condenses. The change in volume is shown by the equation

$$4H(\text{solid}) + O_2 = 2H_2O(\text{liquid}).$$

The gas which disappears is oxygen in the proportion of one molecule for each 4 grm. of hydrogen. The amount of available hydrogen in coals varies from 3 to 5 per cent. so that on a gram sample there would be on an average 0.04 grm. of hydrogen which would unite with 0.01 grm. molecule of oxygen causing a correction of 5 calories—a negligible amount except as it may be considered as balancing other minor errors such as that due to the oxidation of nitrogen. With petroleum the correction will be about three times as great as with coal.

13. Water Value of Calorimeter.—When combustion occurs in a calorimeter there follows a rise in the temperature of both the water and of the calorimeter vessel. It is necessary to find how many calories are required to heat the metal parts of the calorimeter one degree and when this has been accomplished the value is translated for convenience of calculation into grams of water and called the water value of the calorimeter. The water value is usually determined in three ways. The first is by calculation from the weight of the metal parts and their specific heats; the second is by the combustion of a pure substance, such as sugar, benzoic acid or naphthalene, whose heating value is known; and the third is by the addition to the calorimeter of a definite amount of hot water with the determination of the rise in temperature resulting. The first method is simple but of only approximate accuracy. The second method has the advantage of tending to compensate for any errors such as the oxidation of nitrogen in combustion and even errors in the thermometer in so far as these are constant for a series of combustions. The third

method has the advantage of being an absolute one, but it will be found somewhat more difficult of application.

First Method.—The first method requires simply that the weights of each of the several different materials contained in the bomb, the stirrer, the thermometer and the water-containing vessel be known. By multiplying these weights by the specific heats as given in the following table the number of calories is obtained directly.

TABLE OF SPECIFIC HEATS[1]

	Sp. ht.
Tool steel	0.1087
Gun steel	0.1114
German silver	0.094
Platinum	0.032
Lead	0.030
Oxygen (constant vol.)	0.157
Brass	0.094
Mercury	0.033
Glass	0.19

The inaccuracy of the method lies partly in the fact that it is not possible to determine the individual weights of each of these constituents—*e.g.*, the mercury in the thermometer, and partly in the fact that not all of the materials thus weighed are heated in actual practice to the temperature indicated by the thermometer immersed in water. A large part of the thermometer is outside of the calorimeter, a part of the stirrer is constantly passing in and out, and the top of the calorimeter vessel although within the calorimeter is not in contact with the water. On the other hand there is some transfer of heat from the calorimeter vessel to its jackets of which no account is taken. Fortunately all these errors are minor ones but the method can hardly be considered accurate within 3 per cent.

Second Method.—The method of determining the water value of a calorimeter by the combustion of a substance of known heating value is the most commonly employed and the most reliable one. Sugar and benzoic acid are substances which are readily obtained in a state of purity and whose heating value has been determined by a number of independent observers. The U. S. Bureau of Standards considers the following heating values to be the most reliable:

[1] Atwater and Snell, *J. Am. Chem. Soc.*, 25, 694.

Cane sugar	.3945	calories per gram.
Benzoic acid	.6321	calories per gram.
Camphor	.9290	calories per gram.
Naphthalene	.9612	calories per gram.

The values for naphthalene are not very concordant. The heating values per gram as given by different authorities are as follows:

Berthelot	.9692	calories per gram.
Atwater	.9628	calories per gram.
Fischer & Wrede	.9668	calories per gram.

The recent work of Richards and Jesse[1] has shown that very special precautions are necessary for the complete combustion of volatile hydrocarbons, and it is probable that incomplete combustion is in part to blame for the disagreement in the values for naphthalene.

The procedure in determining the water value is exactly the same as for the combustion of a fuel. A sufficient amount of the pure material is pressed into a pellet so that the heat evolved by its combustion will be 7000–8000 calories. This is placed in the bomb which is charged with oxygen, set in the calorimeter and fired, the temperature readings being made as usual. In the final calculations the unknown to be solved for is the mass of water equivalent to the calorimeter which has been heated. The difference between this value and the mass of water actually added gives the water value of the calorimeter.

The method of conducting the combustion is the same as that for coal and should be recorded according to the form, § 8. The following example gives the method of calculation.

Total heat evolved		
from benzoic acid	1.0856 × 6320 = 6860	calories
from iron wire	0.022 × 1600 = 35	
		6895
Corrected rise in temperature 2.854° C.		
Heat absorbed by water 2000 × 2.854	=	5708
Heat absorbed by calorimeter		1187 calories

$$\text{Water value} = \frac{1187}{2.854} = 415$$

[1] *J. Am. Chem. Soc.*, 32, 268 (1910).

The accuracy of this process is dependent first on the purity of the materials used as a standard. Samples of pure substances with certified heat value should be obtained from the Bureau of Standards. The accuracy is also affected by errors in the thermometer, errors due to oxidation of nitrogen, etc., but in this very fact lies one of the valuable points of the method. For if it be assumed that with a thermometer set at a given zero there is an error of 0.02° in a rise of three degrees and that there is a correction of 8 calories to be made with oxygen from a certain tank when a sample of sugar which gives a rise of 3°, is burned, and both of these corrections be neglected, it is evident that the water value obtained will be in error. But if this erroneous water value be used in the calculations of the heating value of a coal where the errors due to the thermometer and the oxidation of nitrogen are the same as in the combustion of sugar, and where the total rise in temperature is approximately the same, the erroneous water value will compensate for the errors on the coal test and the result of the coal test will be correct.

Third Method.—The third method of determining the water value of a calorimeter requires that the instrument, set up as if for a combustion except that there is no water in the calorimeter vessel, be allowed to stand in a room free from draughts and of quite constant temperature until all parts of the instrument have come to a uniform temperature which is correctly indicated by the thermometer. This requires several hours. The same mass of water as used in a regular determination is brought to a temperature approximately three degrees above or below that of the calorimeter and its temperature is accurately observed. This can best be done with the help of the thermometer taken from the calorimeter. If the calorimeter is at room temperature there is no danger of its changing within the few minutes necessary for the next steps. There is a decided danger of change of temperature of the water to be added, and to guard against error it should be kept in a flask as carefully insulated as possible and stirred so as to be of uniform temperature throughout. A vacuum flask or thermos bottle with a wide mouth is excellent. The temperature of the calorimeter and that of the water having been noted the lid of the calorimeter is removed, the water quickly poured in and the mixture stirred, while the

usual temperature observations are made. Part of the heat given off by the water has been used to warm the calorimeter and part has been lost in radiation. The amount of heat received by the calorimeter divided by the rise in temperature gives the water value. This method gives values which are entirely independent of any errors due to impurity in sugar or benzoic acid or to oxidation of nitrogen, etc. If carefully carried out it is a satisfactory method.

This method in its most accurate form imparts a definite amount of heat to the calorimeter electrically, instead of by added hot water. A fine wire coil of known resistance is placed in the calorimeter and an electric current of carefully measured voltage and amperage passed through it for a definite time. The method is used in research laboratories, but is hardly to be considered a technical method, and is not described here in detail.

14. Accuracy of Results.—It is the aim to determine by combustion in the bomb calorimeter the amount of heat which would be evolved by the combustion of a fuel in the outside air. This standard is not an absolute one, for not only will carbon be burned to carbon dioxide and hydrogen to water in an ordinary fire but also sulphur will be burned, in part to SO_2 and in part to SO_3, and small amounts of nitrogen will be burned. In applying corrections to the figures obtained in the bomb calorimeter it is customary to assume that all of the sulphur of the coal burns to SO_3 in the bomb, and that all of it burns to SO_2 in the air, and that no nitrogen is oxidized on combustion of coal in air. The errors introduced by these assumptions are small and are usually neglected. The accuracy of the estimation of the amount of heat evolved by combustion in the bomb will depend on the accuracy with which the water value of the system is known, the care taken in making radiation corrections and the accuracy with which the rise in temperature is measured. This last usually involves the largest error. If the error is 0.01°, it will amount to about 0.3 per cent. or 50 British thermal units. When care is taken in every detail and apparatus of superior quality is used the agreement between duplicate determinations will be closer than this but it is certainly not safe to claim a closer absolute accuracy since according to Jesse[1] the highest

[1] *Jour. Ind. and Eng. Chem.*, 4, 748 (1912).

authorities differ by 0.25 per cent. as to the absolute heating value of sugar and benzoic acid. The Committee on Coal Analysis states that in their judgment results obtained by a single analyst should not differ more than 0.3 per cent. and that results obtained by different analysts should not vary by over 0.4 per cent. This high standard can only be attained when every precaution is observed.

15. Gross and Net Heating Values.—The heating value of the fuel computed by the method given above gives the total heat developed when the water formed condenses to a liquid within the calorimeter. This gives the total amount of heat or the "gross" heat value. In most industrial opperations the water escapes as steam, and if deduction is made for its latent heat, a lower "net" heating value is obtained. This "net" figure gives a closer approximation to the heat which is ordinarily utilized, but it does not give it accurately, because an arbitrary assumption has been made as to the temperature of the escaping gases. It is customary to report the total heating value of the coal and allow the consumer to put such a factor on it as will indicate its relative efficiency for the purpose to which he intends to put it. The method of calculation of net heating values is given in § 12 of Chapter VII on Heating Value of Gas.

CHAPTER XVII

HEATING VALUE OF COAL BY THE PARR CALORIMETER AND OTHER METHODS

1. Introduction.—The preceding chapter was devoted to a discussion of the bomb calorimeter as the standard instrument for the determination of the heating value of coal. The present chapter will deal with other methods, such as combustion in stream of oxygen, combustion with chemicals like sodium peroxide, and calculation of the heating value from the chemical composition of the coal.

2. Combustion in a Stream of Oxygen.—Calorimeters of this type have become obsolete on account of difficulties of manipulation and sources of error. The temperature of the oxygen flowing in must be accurately measured and also the temperature of the gases flowing out, for correction must be made for the heat which these streams of gas carry. The great source of error is the incomplete combustion of the coal. With bituminous coals the smoke may frequently be seen issuing from the instrument and even with anthracite and coke, carbon monoxide may always be found in the escaping gases. Accurate results have been obtained with this type of calorimeter but only after laborious correction for the large number of errors.

3. The Thompson Calorimeter.—A very crude form of calorimeter which has also become obsolete was that of Lewis Thompson. He mixed powdered coal with potassium chlorate and nitrate, placed the mixture in a calorimeter vessel and fired the charge. The method and apparatus were crude throughout but the greatest source of error lay in the heat absorbed in the decomposition of the chlorate and nitrate. When coal burns under a boiler it unites with gaseous oxygen to form CO_2 and H_2O. Essentially the same result takes place in a bomb calorimeter. When, however, the oxygen is taken from one form of chemical combination and is made to combine with the coal to form a different compound, the result is not at all the same as that

obtained in the combustion of the coal with gaseous oxygen and the corrections to be applied must be worked out with great care. Scheurer-Kestner[1] determined that if 15 per cent. was added to the heating value obtained with the Thompson[1] calorimeter, the results never differed by more than 4 per cent. from those obtained by the Favre and Silverman calorimeter which burns the coal in a stream of oxygen.

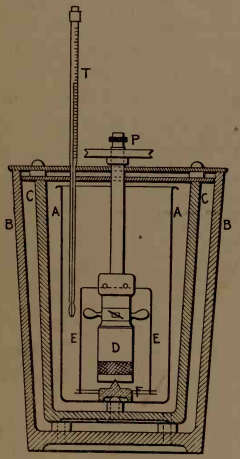

FIG. 46.—Parr calorimeter.

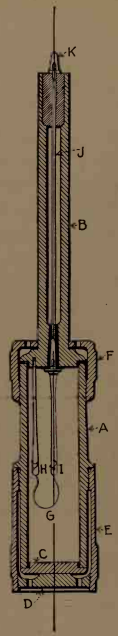

FIG. 47.—Details of Parr calorimeter.

4. The Parr Calorimeter.—Parr[2] proposed sodium peroxide as a chemical to be used in oxidizing coal in a calorimeter, worked out the corrections to be applied, and devised a very practical

[1] *Bull. Soc. Ind.*, Mulhouse, 506, 1888.

[2] *Jour. Am. Chem. Soc.*, 22, 646 (1900).
Jour. Am. Chem. Soc., 24, 167 (1902).
Jour. Am. Chem. Soc., 29, 1606 (1907).
The Chemical Engineer, 6, 253 (1907).
J. Ind. and Eng. Chem., 1, 673 (1909).

calorimeter. He writes the probable reactions in the calorimeter as follows:

$$2Na_2O_2+C=Na_2CO_3+Na_2O$$
$$Na_2O_2+Na_2O+4H+O=4NaOH.$$

There is more heat evolved in each of these reactions than in the combustion of carbon and hydrogen with gaseous oxygen but fortunately the reduction factor is closely the same for both of them. The heat evolved by the combustion of carbon and hydrogen in the Parr calorimeter multiplied by 0.73 gives the true heat value. Smaller corrections are to be made for the dissociation of the $KClO_3$ used, for the oxidation of sulphur, the combustion of the fuse wire, the fusion of the ash, and the hydroxyl or combined water present in coal.

Since the oxygen is introduced as a solid and the Na_2CO_3 and NaOH formed in the reaction are also solids, the bomb need not be made to resist high gas pressures but may be made of thin metal.

The general arrangement of the calorimeter is shown in Fig. 46 where B and C are two fiber buckets acting as heat insulators, A is the can for water, and D the combustion bomb which sits upon a cone F and is rotated by a belt running in the pulley P. The stirring is very effectively accomplished by the removable wings shown attached to the bomb which force the water down the annular space between the bomb and the shell E out of openings at the bottom and up again on the outside.

Details of the bomb are shown in Fig. 47 where A is the brass shell closed at each end by a plate and gasket held in place by a screwed cap. The top plate forms the bottom of the stem B which carries in its center the insulated wire KJI of the firing circuit. The lower cap D together with the sleeve E forms an air chamber around the lower portion of the bomb which prevents too sudden cooling of the fused mass and thus allows time for completion of the reaction.

5. Preparation of Parr Calorimeter.—The bomb must be thoroughly dry and the gaskets in good condition. It is best to dry the parts after each test in an oven and to examine them carefully before putting them together. The lower cap C is fitted into place, the outer sleeve E screwed on and the plug

D screwed firmly down with the wrench provided. Water leaking into the bomb always spoils the determination and may cause an explosion.

The coal is to be ground to pass a 100-mesh sieve in order that it may react rapidly with the peroxide. Anthracite coal, coke, semi-bituminous and eastern bituminous coals in which the moisture will not exceed 3 per cent. may be used in an air-dry condition. Other bituminous coals, lignites, peats, etc., must be dried at 105° C. before use to avoid the reaction between the hygroscopic moisture and the peroxide with evolution of heat in the calorimeter. The danger of change in the coal sample during the processes of drying and grinding is treated in Chapter XV on Chemical Analysis.

It is necessary to secure very intimate mixture of the coal, the Na_2O_2 and the $KClO_3$ added as an accelerator of combustion. Professor Parr recommends that 1 grm. of the dry and finely ground $KClO_3$ be weighed into the bomb first, and to that be added 0.5 grm. of the coal prepared as directed above and that the two be mixed by stirring with a glass rod. To this is added approximately 10 grm. of sodium peroxide which may be measuerd with sufficient accuracy in the scoop provided with the instrument. The contents of the bomb are next to be thoroughly mixed by shaking. If this were done after the regular top and firing wire were in place the firing wire would almost certainly become twisted and short circuited, so it is better to use the false top provided. It is well at the beginning of the shaking process to invert the cartridge and tap it sharply on the desk to dislodge any coal which may have stuck to the bottom. When the mixing is complete the bottom of the cartridge may be tapped lightly against the desk to dislodge any material sticking to the cap. The regular top to which about 4 in. of fine iron wire (32 or 34 American gage) has been attached in a loop as shown at G of Fig. 47 is now placed carefully in position and screwed into place. Care should be taken after this has been adjusted, not to tip the bomb since the fine iron wires are easily crossed. The spring stirring clips may now be adjusted and the apparatus set up as shown in Fig. 46.

The strength of the firing current will vary between 2 and 4 amperes. It should be adjusted by trials in the open air until

the wire fuses promptly on closing the switch. Where electric current for ignition is not available another form of calorimeter head may be used which allows ignition by a hot wire slug dropped through the hollow stem. The specified dimensions of the slug for this purpose are 1 cm. long, and 2.5 mm. diameter. This gives a weight of a little over 0.3 grm. and involves a correction of about .022° F.

6. Care of Sodium Peroxide.—Sodium peroxide is hygroscopic and absorbs moisture from the air, even when preserved in apparently well-stoppered bottles, forming $Na_2O_2.2H_2O$. The effect of this hydrate formation is illustrated by an experiment made by Professor Parr. He exposed 10 grm. of sodium peroxide on a watch glass in the laboratory for an hour and found that it had gained in weight nearly 0.5 grm. This peroxide when used in the calorimeter gave a rise in temperature higher by 0.194° than the pure peroxide. As the total correct rise of temperature in this experiment was only 2.180° it will be seen that the error was almost 9 per cent.

The sodium peroxide should not only be pure and anhydrous but should also be in grains of the proper size. If the peroxide is too coarse the powdered coal tends to sift to the bottom of the bomb and escape combustion. If peroxide is too fine the reaction is sometimes very violent. The manufacturers of the calorimeter furnish reliable peroxide in small hermetically sealed cans and also furnish a clamp-top fruit jar which is said to preserve the contents of a single can during its use.

Sodium peroxide reacts at ordinary temperatures with all organic substances in presence of moisture with evolution of heat often sufficient to produce flame or explosion. Mixtures of sodium peroxide and coal which may have to be disposed of are not to be thrown into waste jars. They may be cautiously and slowly poured into a vessel containing considerable water which will absorb the heat and prevent violent reactions. Sodium peroxide causes bad burns on the skin.

7. Operation of Parr Calorimeter.—The bomb prepared as above directed is placed in the calorimeter vessel and properly centered. Two thousand grams of water are then added to the calorimeter vessel. It is preferable that the temperature of the water should be about 2.0° C. below room temperature for the

radiation correction will be less under these conditions. The thermometer is adjusted and the bomb started to rotating at the rate of about 100 revolutions a minute. Temperatures are to be read at the end of each minute. Within two or three minutes the readings of the thermometer should become almost constant except for the regular and very slight change due to radiation. Should the thermometer rise irregularly and more rapidly than 0.01 or 0.02° per minute during this preliminary period, there is probably a slight leak of water into the bomb. The operation must be at once stopped, the bomb taken out, wiped dry on the outside, opened and emptied. A leaky bomb is not only inaccurate but dangerous. After five readings at intervals of one minute each in the preliminary period have shown only this slight and regular change of temperature, ignition is effected by closing the switch on the cover of the instrument. The thermometer rises very rapidly owing to the thin walls of the bomb and the efficient stirring and usually reaches its maximum after two minutes. Nevertheless observations should be continued for at least eight minutes after ignition to allow corrections for radiation to be made.

The bomb is then removed from the water, wiped dry and opened. There should be no trace of unburned carbon visible, nor any odor. The lower plug is removed and the fused cake in the bottom of the bomb knocked into a casserole containing about 500 c.c. of water. The bomb should also be placed in the water until all the fused peroxide has dissolved. It is then removed, rinsed out and dried.

The solution in the casserole is to be tested for unburned carbon. As an alkaline solution it contains black flakes of oxides of iron and copper. After acidification it becomes a clear yellow solution, with carbon as the only matter in suspension, the silicic acid remaining in solution in the large volume of water. If any unburned carbon is visible it should be filtered on a Monroe or Gooch crucible, dried and weighed. A correction of 8.1 calories must be made for each milligram of unburned carbon. This precaution should never be omitted by a beginner nor where accurate work is important.

The corrected rise of temperature may be calculated according to the formulas given in Chapter XVI, but a simpler method will

usually suffice since this calorimeter is not used where the greatest accuracy is required. It is sufficiently accurate to assume that the average change in temperature per minute during the final period represents also the change due to radiation for each minute during the combustion period. The errors involved in this assumption are small since the temperature in the combustion period rises to almost its full value in the first minute. The temperature at the end of the fourth minute after ignition, may be taken as the end of the combustion period and corrections as shown by the next four minutes' readings, applied to it. Corrections for potassium chlorate, sulphur, ash, etc., as given in the following section are to be deducted from this reading, the result being the corrected final temperature.

The instrument as furnished by the makers has a standard water equivalent of 135 grm. The corrected rise in temperature multiplied by 2135 and by the factor .73 and divided by the weight of the sample in grams gives the heat value in calories per gram. The figure may be converted into British thermal units per pound by multiplying it by 1.8.

8. Corrections to be Applied with Parr Calorimeter.—Parr has worked out very carefully the correction to be applied and published his results in the journals cited as references at the commencement of this chapter. He has shown that the ratio of the heat evolved in the combustion of carbon and hydrogen with gaseous oxygen to that evolved on combustion with sodium peroxide is very closely represented by the factor 0.73. The $KClO_3$ used as an accelerator evolves an additional amount of heat. Similar corrections are required for ash, sulphur, fuse wire, and hydroxyl constituents of the coal. Since the calorimeter is always furnished with a standard water value these corrections may be calculated in terms of temperature. Professor Parr's latest corrections[1] are as follows, the charge being 0.5 grm. coal, 10 grm. Na_2O_2 and 1 grm. $KClO_3$. The corrections are to be subtracted from the observed rise in temperature.

Each per cent. ash is multiplied by.....0.00275° C.
Each per cent. sulphur is multiplied by.....0.005° C.
Correction for heat reaction of $KClO_3$(1.g.) is.....0.130° C.
Heat of combustion of fuse wire (10 mg.) is.....0.008° C.

[1] *J. Ind. and Eng. Chem.*, 1, 673 (1909)

Heat brought in by hot ignition slug is.....0.012
Correction for water of composition in bituminous coals with over 30 per cent. volatile matter is.....0.025° C.

Correction factors for hydroxyl in other substances are as follows, when 0.5 grm. material is taken for combustion.

Brown lignites.....0.050° C.
Wood.....0.111
Sugar.....0.145
Benzoic acid.....0.124

The water value of the calorimeter may be experimentally determined by direct weight of the various parts or by combustion of a pure substance as described in Chapter XVI. The latter method is not so satisfactory as it is with the bomb calorimeter, since it involves the use of the factor 0.73. Benzoic acid and sugar involve also the added correction for hydroxyl.

It is difficult to get ignition of anthracite and coke without adding a small amount of some readily combustible substance such as benzoic acid. The heating value of benzoic acid is 6320 calories per gram and in the Parr calorimeter 0.2 grm. will evolve $\frac{1264}{0.73}$ calories plus the added calories due to its hydroxyl contents. Reducing this to a temperature basis it amounts to 0.811 + 0.050° C. = 0.861° C. to be subtracted in case 0.2 grm. benzoic acid is used as an igniter.

9. Accuracy of Parr Calorimeter.—The work of Professor Parr has shown definitely that accurate results may be obtained with this calorimeter, but it has also shown that this accuracy can be gained only by the observation of precautions and the use of corrections which deprive the process of much of the simplicity which formerly characterized it. Accurate results are dependent on the quality of the peroxide used, a point which must usually be taken on faith. The calculations involve a knowledge of the ash, sulphur, and volatile matter of the coal, and the application of corrections for these constituents. These points prevent the method from being a standard one as is combustion in the bomb calorimeter, but do not prevent it from being a useful commercial instrument where the highest accuracy is not required.

10. Calculation of the Heating Value from Chemical Analysis— If an ultimate analysis is available, the heating value of a coal

may be calculated with fair accuracy from the Dulong formula which is usually given as

$$\text{Calorific power} = \frac{8080\,\text{C} + 34460\,(\text{H} - \frac{\text{O}}{8}) + 2500\,\text{S}}{100}$$

where C, H, O and S represent the respective percentages of these various elements shown by the analysis. This formula gives results in Calories per kilogram which when multiplied by 1.8 are converted into British thermal units per pound. Tests of 57 coals made by the U. S. Geological Survey[1] show an average error of 87.5 calories in the calculated result and a maximum error of 312 calories. Inasmuch as it is much simpler to determine the calorific value directly than to make an ultimate analysis, the value of this formula has come to lie largely in its confirmation of the correctness of the ultimate analysis.

A formula which would correlate proximate analysis and heating value would be much more useful, but on account of the variable composition of the volatile matter in different types of coal no general formula can be devised which will fit all cases. The combustible matter of coal from a given seam is, however, quite constant in composition and after its value has been experimentally determined this figure may be used with considerable accuracy as a basis for the calculation of the heating value of similar coals whose moisture and ash content are known.

[1] *U. S. G. S.*, Professional Paper 48 (1906); *Bulletin* 382 (1909) p. 24.

TABLE I.—SATURATION PRESSURE OF WATER VAPOR

From 0–50° C. in millimeters of mercury. Scheel and Heuse, *Ann. d. Phys.* (4), 31, 731 (1910).

Temp.	mm. Hg.	Temp.	mm. Hg.
0	4.579	26	25.217
1	4.926	27	26.747
2	5.294	28	28.358
3	5.685	29	30.052
4	6.101	30	31.834
5	6.543	31	33.706
6	7.014	32	35.674
7	7.514	33	37.741
8	8.046	34	39.911
9	8.610	35	42.188
10	9.210	36	44.577
11	9.845	37	47.082
12	10.519	38	49.708
13	11.233	39	52.459
14	11.989	40	55.341
15	12.790	41	58.36
16	13.637	42	61.52
17	14.533	43	64.82
18	15.480	44	68.28
19	16.481	45	71.90
20	17.539	46	75.67
21	18.655	47	79.62
22	19.832	48	83.74
23	21.074	49	88.05
24	22.383	50	92.54
25	23.763		

TABLE II.—REDUCTION OF GAS VOLUMES TO 0° AND 760 MM. MERCURY PRESSURE AND DRYNESS

If the gas is already dry the reduction formula is

$$V_0 = \frac{V}{1+.00367\ t} \frac{h}{760}$$

where t is the temperature and h the barometric pressure corresponding to the volume V.

If the gas is saturated with moisture there must be deducted from the observed barometric reading the value e for the vapor pressure of water corresponding to the temperature t as given in Table I. The reduction formula then becomes

$$V_0 = \frac{V}{1+.00367\ t} \frac{h-e}{760}$$

The following table gives the values for 1+0.00367t for each degree from 0° to 50° C.

t	1+0.00367t	t	1+0.00367t
0	1.00000	26	1.09542
1	1.00367	27	1.09909
2	1.00734	28	1.10276
3	1.01101	29	1.10643
4	1.01468	30	1.11010
5	1.01835	31	1.11377
6	1.02202	32	1.11744
7	1.02569	33	1.12111
8	1.02936	34	1.12478
9	1.03303	35	1.12845
10	1.03670	36	1.13212
11	1.04037	37	1.13579
12	1.04404	38	1.13946
13	1.04771	39	1.14313
14	1.05138	40	1.14680
15	1.05505	41	1.15047
16	1.05872	42	1.15414
17	1.06239	43	1.15781
18	1.06606	44	1.16148
19	1.06973	45	1.16515
20	1.07340	46	1.16882
21	1.07707	47	1.17249
22	1.08074	48	1.17616
23	1.08441	49	1.17983
24	1.08808	50	1.18350
25	1.09175		

TABLE III.—FACTORS FOR REDUCTION OF GAS VOLUME TO 60° F. AND 30 IN. OF MERCURY PRESSURE AND SATURATION WITH MOISTURE

TEMPERATURE °F.	BAROMETER																			
	28.6	28.7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
107	0.816	0.820	0.823	0.826	0.829	0.832	0.835	0.838	0.841	0.844	0.847	0.851	0.854	0.857	0.860	0.864	0.867	0.870	0.874	0.877
106	0.820	0.823	0.826	0.829	0.832	0.835	0.838	0.841	0.844	0.847	0.851	0.854	0.857	0.860	0.863	0.867	0.870	0.874	0.878	0.881
105	0.823	0.827	0.830	0.833	0.836	0.839	0.842	0.845	0.848	0.851	0.855	0.858	0.861	0.864	0.867	0.871	0.874	0.878	0.881	0.884
104	0.827	0.830	0.833	0.836	0.839	0.842	0.845	0.848	0.851	0.854	0.858	0.861	0.864	0.867	0.871	0.874	0.878	0.881	0.884	0.887
103	0.830	0.834	0.837	0.840	0.843	0.847	0.849	0.852	0.855	3.858	0.862	0.865	0.868	0.871	0.874	0.878	0.881	0.885	0.888	0.891
102	0.834	0.837	0.840	0.843	0.847	0.850	0.853	0.856	0.859	0.862	0.865	0.868	0.871	0.874	0.878	0.881	0.885	0.888	0.891	0.894
101	0.837	0.840	0.843	0.846	0.850	0.853	0.856	0.859	0.862	0.865	0.868	0.872	0.875	0.878	0.882	0.885	0.888	0.891	0.895	0.898
100	0.840	0.843	0.846	0.849	0.853	0.856	0.859	0.862	0.865	0.868	0.872	0.875	0.878	0.881	0.885	0.888	0.891	0.895	0.898	0.901
99	0.844	0.847	0.850	0.853	0.857	0.860	0.863	0.866	0.869	0.872	0.876	0.879	0.882	0.885	0.889	0.892	0.895	0.898	0.902	0.905
98	0.847	0.850	0.853	0.856	0.860	0.863	0.866	0.869	0.872	0.875	0.879	0.882	0.885	0.888	0.892	0.895	0.898	0.902	0.905	0.908
97	0.850	0.853	0.856	0.859	0.863	0.866	0.870	0.873	0.876	0.879	0.882	0.885	0.888	0.891	0.894	0.898	0.901	0.905	0.908	0.911
96	0.854	0.857	0.860	0.863	0.867	0.870	0.873	0.876	0.879	0.882	0.886	0.889	0.892	0.895	0.898	0.901	0.904	0.908	0.911	0.914
95	0.857	0.860	0.863	0.866	0.870	0.873	0.876	0.879	0.882	0.885	0.889	0.892	0.895	0.898	0.901	0.904	0.908	0.911	0.914	0.918
94	0.860	0.863	0.866	0.869	0.873	0.876	0.879	0.882	0.885	0.888	0.892	0.895	0.898	0.901	0.904	0.907	0.911	0.914	0.918	0.921
93	0.863	0.866	0.869	0.872	0.876	0.879	0.883	0.886	0.889	0.891	0.895	0.898	0.901	0.904	0.907	0.910	0.914	0.918	0.921	0.924
92	0.866	0.869	0.872	0.875	0.879	0.882	0.885	0.889	0.892	0.894	0.898	0.902	0.904	0.907	0.910	0.914	0.917	0.921	0.924	0.928
91	0.869	0.872	0.875	0.879	0.882	0.885	0.889	0.892	0.895	0.898	0.902	0.905	0.908	0.911	0.914	0.917	0.921	0.924	0.928	0.931
90	0.872	0.875	0.878	0.881	0.885	0.888	0.892	0.895	0.898	0.901	0.905	0.908	0.911	0.914	0.917	0.920	0.924	0.927	0.931	0.934
89	0.875	0.878	0.882	0.885	0.889	0.892	0.895	0.898	0.901	0.904	0.907	0.910	0.914	0.917	0.920	0.923	0.927	0.931	0.934	0.937
88	0.878	0.881	0.885	0.888	0.892	0.895	0.898	0.901	0.904	0.907	0.910	0.913	0.917	0.920	0.923	0.926	0.930	0.934	0.937	0.940
87	0.881	0.884	0.888	0.891	0.895	0.898	0.901	0.904	0.907	0.910	0.913	0.916	0.920	0.923	0.926	0.929	0.933	0.937	0.940	0.943
86	0.884	0.887	0.890	0.894	0.898	0.901	0.904	0.907	0.910	0.913	0.916	0.919	0.923	0.926	0.929	0.932	0.936	0.940	0.943	0.946
85	0.887	0.890	0.893	0.896	0.900	0.903	0.906	0.909	0.913	0.916	0.919	0.922	0.926	0.929	0.932	0.936	0.939	0.943	0.946	0.949
84	0.889	0.893	0.896	0.899	0.903	0.906	0.909	0.912	0.915	0.919	0.922	0.925	0.928	0.932	0.935	0.939	0.942	0.946	0.949	0.952
83	0.892	0.895	0.899	0.902	0.906	0.909	0.912	0.915	0.918	0.921	0.924	0.928	0.931	0.935	0.938	0.942	0.945	0.949	0.952	0.955
82	0.895	0.898	0.901	0.905	0.908	0.911	0.914	0.918	0.921	0.924	0.927	0.931	0.934	0.937	0.941	0.945	0.948	0.951	0.954	0.958
81	0.898	0.901	0.905	0.908	0.911	0.914	0.917	0.921	0.924	0.927	0.930	0.934	0.937	0.940	0.944	0.948	0.951	0.954	0.957	0.960

TABLE III.—FACTORS FOR REDUCTION OF GAS VOLUME TO 60° F. AND 30 IN. OF MERCURY PRESSURE AND SATURATION WITH MOISTURE.—(*Continued*)

TEMPERATURE °F.	BAROMETER																		
	28.6	28.7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
80	0.901	0.904	0.907	0.910	0.914	0.917	0.920	0.923	0.927	0.930	0.933	0.937	0.940	0.943	0.946	0.950	0.954	0.957	0.960	0.963
79	0.904	0.907	0.910	0.914	0.917	0.920	0.923	0.926	0.930	0.933	0.936	0.939	0.943	0.946	0.949	0.953	0.956	0.960	0.963	0.967
78	0.906	0.909	0.913	0.916	0.919	0.923	0.926	0.929	0.932	0.936	0.939	0.942	0.946	0.949	0.952	0.956	0.959	0.962	0.966	0.969
77	0.909	0.912	0.915	0.919	0.922	0.925	0.928	0.931	0.935	0.938	0.942	0.945	0.948	0.951	0.955	0.958	0.962	0.965	0.968	0.972
76	0.911	0.915	0.918	0.921	0.925	0.928	0.931	0.935	0.938	0.941	0.944	0.948	0.951	0.954	0.958	0.961	0.964	0.968	0.971	0.975
75	0.914	0.917	0.921	0.924	0.928	0.931	0.934	0.937	0.940	0.943	0.947	0.950	0.954	0.957	0.960	0.963	0.967	0.971	0.974	0.978
74	0.917	0.920	0.924	0.927	0.930	0.933	0.937	0.940	0.943	0.957	0.950	0.953	0.957	0.960	0.963	0.966	0.970	0.973	0.977	0.980
73	0.920	0.923	0.926	0.930	0.933	0.936	0.940	0.943	0.946	0.949	0.953	0.956	0.960	0.963	0.966	0.969	0.972	0.976	0.980	0.983
72	0.922	0.925	0.929	0.932	0.935	0.939	0.942	0.945	0.949	0.952	0.955	0.959	0.962	0.965	0.968	0.972	0.975	0.979	0.982	0.986
71	0.925	0.928	0.931	0.935	0.938	0.941	0.945	0.948	0.951	0.954	0.958	0.961	0.965	0.968	0.971	0.975	0.978	0.981	0.985	0.989
70	0.927	0.931	0.934	0.937	0.941	0.944	0.947	0.950	0.954	0.957	0.960	0.964	0.967	0.970	0.974	0.977	0.980	0.984	0.988	0.991
69	0.930	0.933	0.937	0.940	0.944	0.947	0.950	0.953	0.957	0.960	0.963	0.967	0.970	0.973	0.977	0.980	0.983	0.987	0.990	0.994
68	0.932	0.936	0.939	0.942	0.946	0.949	0.952	0.956	0.959	0.962	0.966	0.969	0.972	0.976	0.979	0.983	0.986	0.989	0.993	0.997
67	0.935	0.938	0.942	0.945	0.949	0.952	0.955	0.959	0.962	0.965	0.968	0.972	0.975	0.979	0.982	0.985	0.989	0.992	0.996	1.000
66	0.938	0.941	0.944	0.948	0.951	0.954	0.958	0.961	0.964	0.968	0.971	0.974	0.978	0.981	0.985	0.988	0.992	0.995	0.998	1.002
65	0.941	0.944	0.947	0.950	0.954	0.957	0.960	0.963	0.967	0.970	0.973	0.977	0.980	0.984	0.987	0.991	0.994	0.997	1.001	1.005
64	0.943	0.946	0.949	0.953	0.956	0.959	0.963	0.966	0.969	0.973	0.976	0.980	0.983	0.986	0.990	0.994	0.997	1.000	1.004	1.008
63	0.945	0.949	0.952	0.955	0.959	0.962	0.965	0.969	0.972	0.975	0.979	0.982	0.985	0.989	0.993	0.996	1.000	1.003	1.006	1.010
62	0.947	0.951	0.954	0.958	0.961	0.964	0.968	0.971	0.975	0.978	0.981	0.985	0.988	0.991	0.995	0.999	1.002	1.005	1.009	1.013
61	0.950	0.954	0.957	0.961	0.964	0.967	0.971	0.974	0.977	0.981	0.984	0.987	0.991	0.994	0.998	1.001	1.005	1.008	1.011	1.015
60	0.952	0.956	0.959	0.963	0.966	0.969	0.973	0.976	0.980	0.983	0.986	0.990	0.993	0.997	1.000	1.004	1.007	1.010	1.014	1.017
59	0.955	0.959	0.962	0.966	0.969	0.972	0.976	0.979	0.983	0.986	0.989	0.992	0.995	0.999	1.003	1.006	1.010	1.013	1.016	1 020
58	0.957	0.961	0.964	0.968	0.971	0.975	0.978	0.981	0.985	0.988	0.992	0.995	0.998	1.002	1.005	1.009	1.012	1.016	1.019	1.023
57	0.960	0.963	0.967	0.970	0.974	0.977	0.980	0.984	0.988	0.991	0.994	0.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025
56	0.962	0.966	0.969	0.973	0.976	0.979	0.982	0.986	0.990	0.993	0.996	1.000	1.003	1.007	1.010	1.014	1.017	1.021	1.024	1.028
55	0.965	0.968	0.972	0.975	0.979	0.982	0.985	0.989	0.993	0.996	0.999	1.002	1.006	1.009	1.013	1.016	1.020	1.023	1.027	1.030
54	0.967	0.970	0.974	0.977	0.981	0.984	0.988	0.991	0.995	0.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033

TABLE III.—FACTORS FOR REDUCTION OF GAS VOLUME TO 60° F. AND 30 IN. OF MERCURY PRESSURE AND SATURATION WITH MOISTURE.—(*Continued*)

TEMPERATURE °F.	BAROMETER																			
	28.6	28.7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
53	0.969	0.973	0.976	0.980	0.983	0.986	0.990	0.993	0.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.031	1.035
52	0.971	0.975	0.978	0.982	0.985	0.989	0.992	0.996	0.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038
51	0.974	0.977	0.981	0.984	0.988	0.991	0.995	0.998	1.002	1.005	1.009	1.012	1.016	1.019	1.023	1.026	1.030	1.033	1.037	1.040
50	0.976	0.980	0.983	0.987	0.990	0.994	0.997	1.001	1.004	1.008	1.011	1.015	1.018	1.022	1.025	1.029	1.032	1.036	1.039	1.043
49	0.979	0.982	0.986	0.989	0.993	0.996	1.000	1.003	1.007	1.010	1.014	1.017	1.021	1.024	1.028	1.031	1.035	1.038	1.042	1.045
48	0.981	0.985	0.988	0.992	0.995	0.999	1.002	1.006	1.009	1.013	1.016	1.020	1.023	1.027	1.030	1.034	1.037	1.041	1.044	1.048
47	0.984	0.987	0.991	0.994	0.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033	1.036	1.040	1.043	1.047	1.050
46	0.986	0.990	0.993	0.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.032	1.035	1.039	1.042	1.046	1.049	1.053
45	0.989	0.992	0.996	0.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038	1.041	1.045	1.048	1.052	1.056
44	0.991	0.994	0.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033	1.036	1.040	1.043	1.047	1.050	1.054	1.058
43	0.993	0.997	1.001	1.004	1.008	1.011	1.015	1.018	1.022	1.025	1.029	1.032	1.036	1.039	1.043	1.046	1.050	1.053	1.057	1.060
42	0.995	0.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038	1.041	1.045	1.048	1.052	1.055	1.059	1.063
41	0.998	1.001	1.005	1.009	1.012	1.016	1.019	1.023	1.026	1.030	1.034	1.037	1.041	1.044	1.048	1.051	1.055	1.058	1.062	1.065
40	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.032	1.036	1.039	1.043	1.046	1.050	1.053	1.057	1.060	1.064	1.068
39	1.002	1.006	1.010	1.013	1.017	1.020	1.024	1.028	1.031	1.035	1.038	1.042	1.045	1.049	1.052	1.056	1.059	1.063	1.066	1.070
38	1.005	1.009	1.012	1.016	1.020	1.023	1.027	1.030	1.034	1.037	1.041	1.044	1.048	1.051	1.055	1.058	1.062	1.065	1.069	1.073
37	1.007	1.011	1.015	1.018	1.022	1.025	1.029	1.032	1.036	1.039	1.043	1.046	1.050	1.053	1.057	1.060	1.064	1.068	1.072	1.076
36	1.009	1.013	1.017	1.020	1.024	1.027	1.031	1.035	1.038	1.042	1.045	1.049	1.052	1.056	1.060	1.063	1.067	1.071	1.074	1.078
35	1.012	1.015	1.019	1.022	1.026	1.030	1.033	1.037	1.041	1.044	1.048	1.051	1.055	1.058	1.062	1.065	1.069	1.073	1.077	1.081
34	1.014	1.018	1.022	1.025	1.029	1.032	1.036	1.040	1.043	1.047	1.050	1.054	1.057	1.061	1.064	1.068	1.072	1.075	1.079	1.083
33	1.016	1.020	1.024	1.027	1.031	1.034	1.038	1.042	1.046	1.049	1.053	1.056	1.060	1.063	1.067	1.070	1.074	1.078	1.082	1.086
32	1.019	1.023	1.027	1.030	1.034	1.037	1.041	1.044	1.048	1.051	1.055	1.058	1.062	1.066	1.069	1.073	1.077	1.081	1.085	1.089
31	1.021	1.025	1.029	1.032	1.036	1.039	1.043	1.047	1.050	1.054	1.057	1.061	1.064	1.068	1.072	1.075	1.079	1.083	1.087	1.091
30	1.023	1.027	1.031	1.034	1.038	1.042	1.045	1.049	1.053	1.056	1.060	1.063	1.067	1.071	1.074	1.078	1.082	1.086	1.090	1.094

TABLE IV.—RELATIVE HUMIDITY

As determined from readings of wet and dry bulb thermometer. Calculated for barometric pressure of 29.0 in. of mercury. See §7 of Chapter XIV.

All temperatures in Fahrenheit degrees.

Air temp.	Depression of wet bulb thermometer (t–t′)																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
30	89	78	68	57	47	37	27	17	8	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
35	91	82	73	64	55	46	37	29	20	12	4	....	....	....	....	....	....	....	....	....	....	....	....	....	....
40	92	84	76	68	61	53	46	38	31	23	16	9	2	....	....	....	....	....	....	....	....	....	....	....	....
45	93	86	79	71	65	58	52	45	39	33	26	20	14	8	2	....	....	....	....	....	....	....	....	....	....
50	93	87	81	74	68	62	56	50	44	39	33	28	22	17	12	7	2	....	....	....	....	....	....	....	....
55	94	88	82	76	71	65	60	55	49	44	39	34	29	25	20	15	11	6	2	....	....	....	....	....	....
60	94	89	84	78	73	68	63	58	53	49	44	40	35	31	27	22	18	14	10	6	2	....	....	....	....
65	95	90	85	80	75	70	66	62	57	53	48	44	40	36	32	28	25	21	17	13	10	7	3	....	....
70	95	90	86	81	77	72	68	64	60	56	52	48	44	40	37	33	30	26	23	20	17	13	10	7	4
75	96	91	87	82	78	74	70	66	63	59	55	51	48	44	41	38	34	31	28	25	22	19	16	13	11
80	96	91	87	83	79	76	72	68	64	61	57	54	51	47	44	41	38	35	32	29	27	24	21	18	16
85	96	92	88	84	80	77	74	70	66	63	60	57	54	50	47	44	41	39	36	33	31	28	25	23	20
90	96	92	89	85	81	78	75	71	68	65	62	59	56	53	50	47	44	42	39	37	34	32	29	27	24
95	96	93	89	86	82	79	76	73	70	66	64	61	58	55	52	50	47	45	42	40	37	35	32	30	28
100	96	93	90	86	83	80	77	74	71	68	65	62	59	57	54	52	49	47	44	42	40	37	35	33	31
105	97	93	90	87	84	81	78	75	72	69	66	64	61	59	56	54	51	49	46	44	42	40	38	36	34
110	97	94	90	87	84	81	78	76	73	70	67	65	62	60	57	55	53	50	48	46	44	42	40	38	36
115	97	94	91	88	85	82	79	77	74	71	69	66	64	61	59	57	55	52	50	48	46	44	42	40	38
120	97	94	91	88	85	82	80	77	74	72	69	67	65	62	60	58	56	54	51	49	47	46	44	42	40

TABLE IV.—RELATIVE HUMIDITY.—(*Continued*)

All temperatures in Fahrenheit degrees.

Air temp.	Depression of wet bulb thermometer (t–t′)																							
	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
75	8	5	2	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
80	13	11	8	6	4	1	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
85	18	16	13	11	9	7	5	3	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
90	22	20	18	16	14	12	10	8	6	4	2	....	....	....	....	....	....	....	....	....	....	....	....	....	....
95	26	24	22	20	18	16	14	12	10	9	7	6	3	2	1	....	....	....	....	....	....	....	....	....	....
100	29	27	25	23	21	19	18	16	14	12	11	9	7	6	4	3	1	....	....	....	....	....	....	....	....
105	32	30	28	26	24	22	21	19	17	16	14	13	11	10	8	7	5	4	3	2	....	....	....	....	....
110	34	32	30	29	27	25	24	22	20	19	17	16	14	13	11	10	9	7	6	5	4	3	1	....	....
115	36	34	33	31	29	28	26	25	23	22	20	19	17	16	14	13	12	10	9	8	7	6	5	3	3
120	38	36	35	33	31	30	28	27	25	24	22	21	20	18	17	16	15	13	12	11	10	9	8	6	5

TABLE V.—MEAN SPECIFIC HEATS OF GASES AT CONSTANT PRESSURE IN B.T.U. PER CUBIC FOOT AT 60° F. AND 30 IN. OF MERCURY CALCULATED FOR THE INTERVAL 60° F.–T

T, deg. F.	Carbon dioxide	Water vapor	Nitrogen, oxygen and other diatomic gases
200	0.0237	0.0220	0.0174
400	0.0246	0.0220	0.0175
600	0.0253	0.0221	0.0177
800	0.0260	0.0222	0.0178
1000	0.0268	0.0224	0.0180
1200	0.0275	0.0226	0.0181
1400	0.0282	0.0229	0.0183
1600	0.0287	0.0232	0.0184
1800	0.0292	0.0236	0.0186
2000	0.0298	0.0240	0.0187
2200	0.0302	0.0245	0.0189
2400	0.0306	0.0250	0.0190
2600	0.0309	0.0256	0.0192
2800	0.0312	0.0263	0.0194
3000	0.0314	0.0270	0.0196

TABLE VI.—MEAN SPECIFIC HEATS OF GASES AT CONSTANT PRESSURE IN B.T.U. PER POUND CALCULATED FOR THE INTERVAL 60° F.–T

T	Carbon dioxide	Water vapor	Nitrogen
200° F.	0.2067	0.4653	0.2365
400° F.	0.2143	0.4657	0.2386
600° F.	0.2216	0.4673	0.2407
800° F.	0.2285	0.4698	0.2428
1000° F.	0.2348	0.4735	0.2449
1200° F.	0.2406	0.4782	0.2470
1400° F.	0.2462	0.4841	0.2491
1600° F.	0.2512	0.4910	0.2512
1800° F.	0.2559	0.4990	0.2534
2000° F.	0.2601	0.5081	0.2555
2200° F.	0.2638	0.5182	0.2576
2400° F.	0.2670	0.5294	0.2597
2600° F.	0.2698	0.5420	0.2618
2800° F.	0.2722	0.5557	0.2639
3000° F.	0.2742	0.5702	0.2660

TABLE VII.—VOLUME OF WATER VAPORS TAKEN UP BY ONE CUBIC FOOT OF AIR WHEN SATURATED AT VARIOUS TEMPERATURES

Temperature	Cubic feet of water vapor
0° F.	0.001
12° F.	0.002
22° F.	0.004
32° F.	0.006
42° F.	0.009
52° F.	0.013
62° F.	0.019
72° F.	0.027
82° F.	0.038
92° F.	0.053
102° F.	0.073

TABLE VIII.—COMPARISON OF THE BAUME SCALE FOR LIQUIDS LIGHTER THAN WATER AND SPECIFIC GRAVITIES

Degrees Baumé	Specific gravity	Degrees Baumé	Specific gravity	Degrees Baumé	Specific gravity
10	1.0000	36	0.8433	62	0.7290
11	0.9929	37	0.8383	63	0.7253
12	0.9859	38	0.8333	64	0.7216
13	0.9790	39	0.8284	65	0.7179
14	0.9722	40	0.8235	66	0.7142
15	0.9655	41	0.8187	67	0.7106
16	0.9589	42	0.8139	68	0.7070
17	0.9523	43	0.8092	69	0.7035
18	0.9459	44	0.8045	70	0.7000
19	0.9395	45	0.8000	71	0.6990
20	0.9333	46	0.7954	72	0.6956
21	0.9271	47	0.7909	73	0.6923
22	0.9210	48	0.7865	74	0.6889
23	0.9150	49	0.7821	75	0.6829
24	0.9090	50	0.7777	76	0.6823
25	0.9032	51	0.7734	77	0.6789
26	0.8974	52	0.7692	78	0.6756
27	0.8917	53	0.7650	79	0.6722
28	0.8860	54	0.7608	80	0.6666
29	0.8805	55	0.7567	81	0.6656
30	0.8750	56	0.7526	82	0.6619
31	0.8695	57	0.7486	83	0.6583
32	0.8641	58	0.7446	84	0.6547
33	0.8588	59	0.7407	85	0.6511
34	0.8536	60	0.7368	90	0.6363
35	0.8484	61	0.7329	95	0.6222

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